

ELECTRONIC AND DYNAMICAL ASPECTS
OF DIATOMIC SYSTEMS

By

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Dedicated to

My Parents,

who, though familiar with little of what is reported here,
nonetheless know what I have been doing
and have supported me in it.

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PREFACE

I find it appropriate to make some remarks concerning the perspective and context in which the work reported in this dissertation has been carried out.

Since its inception in the 1920's, Quantum Mechanics has become well established as the suitable framework within which to describe phenomena of a physical and chemical nature. Building upon only a few axioms, the formal Quantum Theory manifests itself in the form of mathematical equations, the solutions to which determine expressions for calculating physically observable quantities. Confidence in Quantum Mechanics derives from the impressive successes it has had in providing results in agreement with experiments. However, in applying Quantum Mechanics to describe actual, known, physical and chemical phenomena, one quickly becomes aware of the fact that there are only a few cases where an exact treatment has been possible. In nearly all cases of interest, the mathematical equations of the theory, though succinct in what they say, are unmanageable to solve. Computational considerations, therefore, have strongly influenced theoretical investigations in physics and chemistry.

Basically two approaches have evolved. The so-called *ab initio* calculations provide approximate solutions to

the "exact" quantum mechanical equations within a framework which, in principle, allows for the solutions to be progressively improved upon to approach the "exact" solutions. One is presumably limited here only by the size of the electronic computer available. On the other hand, one may focus on the main features of some particular physical phenomena of interest, and use the "exact" quantum mechanical equations only as a guide in order to arrive at approximate equations which mimic the important aspects of the process being studied. These approximate, or model, equations are many times only approximately solved! Such apparently crude approaches require of the researcher all of the physical intuition which can be mustered, in order to properly assess the important features of the physical situation and to approximate them reasonably well. Nevertheless, much physical insight and many useful quantitative results can be extracted from this point of view. Indeed, the task of science is essentially to formulate descriptive statements, both qualitative and quantitative, which conform as nearly as possible to the laws and phenomena of nature as we observe them.

Finally, it should be mentioned that there are formal results coming out of quantum theoretical investigations which determine many characteristics of the "exact" and approximate solutions, even before they have been calcu-

lated. Both types of investigations described above rely upon these formal results as well as upon each other. In the dissertation which follows, research of the second type mentioned above will be reported in the form of a quantum mechanical investigation of electronic and dynamical aspects of diatomic systems.

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ELECTRONIC AND DYNAMICAL ASPECTS
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Diatomic systems are considered from the points of view of their electronic structure and the dynamics of motion of the heavy particles (nuclei) upon collision. In Chapter I the electronic and nuclear motions are treated formally by expressing the Schrödinger equation for the nuclei and electrons in independent variables in the body-fixed (BF), center of mass of the nuclei, frame, and then introducing an expansion in terms of a complete set of electronic states at each internuclear separation, R . Born-Oppenheimer and Coulomb couplings between the electronic and nuclear motions are pointed out and discussed.

In Chapter II, atom-atom interaction potentials and electronic structure are investigated using the Multiple Scattering (MS) calculational scheme with the so-called $X\alpha$ approximation to electronic exchange. The atom pairs,

He-He, He-Ar and Ar-Ar are studied, and results are presented for ground and excited state configurations. The computed interaction potentials exhibit Born-Mayer repulsion, and the calculations demonstrate how X α orbital energies can be used to predict crossings between interaction potentials. An analysis is presented of the X α theory and its usefulness for the understanding of collision phenomena.

In Chapter III, Penning ionization (PI) and associative ionization (AI) processes are considered in terms of molecular orbital (MO) correlation diagrams. MO correlation diagrams are calculated for He*(1s2s) + Ar(3p⁶) and He(1s²) + Ar⁺(3p⁵) within the MSX α scheme for non-spin-polarized and spin-polarized orbitals. The ionization process is discussed in terms of an Auger type mechanism involving MO's which can be inspected in the united-atoms (UA) limit in a way which permits an analysis of the angular momentum contributions of the emitted electron in the BF frame. MO correlation diagrams are constructed based on atomic orbital energies at the separated- and united-atoms limits, which are determined from data available in the literature on ground state atomic orbital energies. Estimated MO correlation diagrams are presented for He*(1s2s) + Ar(3p⁶), + Kr(4p⁶), + Hg(6s²), and Ne*(2p⁵3s) + Ar(3p⁶), and in each case an analysis is made of the angular momentum components of the emitted electron. The results confirm that relatively few such components are important for electrons emitted in

PI and AI. The UA analysis shows the importance of spin-polarized MO's, and also Born-Oppenheimer rotational couplings, particularly between MO's which converge to the same UA limit.

In Chapter IV consideration is given to the dynamics involved in collisional ionization processes. The formal development of Chapter I is extended to include both discrete and continuum internal electronic states. The resulting continuously infinite set of coupled equations is then discretized, leading to modified coupled equations for the heavy particle motion. Discretization provides a suitable framework in which to introduce physically reasonable approximations which lead to a treatment of PI and AI in terms of several (≈ 20) two-state coupled equations. Application is made to PI of Ar by $\text{He}^*(1s2s, {}^3S)$, and the results show that the approach includes the important dynamical features. Partial ionization cross-sections per unit energy, ϵ , of the emitted electron are calculated as a function of ϵ , and they show an ϵ dependence in good qualitative and quantitative agreement with experimentally measured energy distributions of emitted electrons. Partial cross-section contributions for the heavy particles in specific angular momentum states are also singled out. Their behavior as a function of ϵ , or of the angular momentum partial wave number, shows structure which reflects regions of high density of states in the continuum of final relative motion

of the heavy particles. The He-Ar metastable and molecular ion potentials are represented by a convenient functional form describing atom-atom interaction potentials over the entire range of R . In addition, the connection between the decay width Γ and the coupling matrix elements between discrete and continuum electronic states is used to make reasonable estimates of the latter from semiempirical results for Γ .

CHAPTER I

INTRODUCTION

The overall subject of this dissertation is the study of electronic and dynamical aspects of diatomic systems. In such a study it is the behavior of the electrons and nuclei, during collision processes of the two atoms comprising the diatomic, which is of interest. In this introductory chapter the collision processes will be discussed formally in terms of the Schrödinger equation which is satisfied by the wave function for the system of nuclei and electrons. The Schrödinger equation will be treated in the body-fixed, center of mass of the nuclei, frame by properly transforming the Hamiltonian operator and wave function to be expressed in this reference frame. The coupled equations will be derived with attention focused on the various sources of coupling between the electronic and nuclear motions.

In the following chapter, matters specifically concerning the electronic structure of some diatoms comprised of rare gas atoms will be considered, and possible applications to collision processes discussed. In Chapter III special attention will be given to chemi-ionization processes involving collisions in which one of the atoms is initially

in an excited state. Features of the electronic structure of such collisions will be discussed, on the basis of which an analysis of the angular momentum contributions to electrons emitted in such processes will be carried out. Finally, in Chapter IV, the dynamics of a specific chemi-ionization process, that of Penning ionization of Argon by metastable Helium, will be treated by means of numerically solving the coupled equations within a two-state approximation. Total and partial cross-sections obtained from the calculations will be reported.

1. A Formal Statement of the Problem

In the quantum mechanical treatment of the two nuclei and N electrons which constitute a diatomic system, the Hamiltonian operator expresses all of the energy contributions associated with the nuclei and electrons. The actual form of the Hamiltonian depends upon the coordinate frame with respect to which the positions of the nuclei and electrons are located. The coordinate frame of most practical use in terms of measuring the results of collision events is one fixed in the laboratory, referred to as the laboratory-fixed (LF) frame. The description of the collision events, however, is most conveniently carried out in a coordinate frame whose origin is fixed to the center of mass of the nuclei (CMN) of the two atoms which are

colliding. The reader is referred elsewhere (see, for example, Pa68 and references therein, and Ju75) for a detailed discussion of various coordinate frames commonly used and the form the Hamiltonian assumes under transformation from one to the other. The formal development in this chapter begins with the Hamiltonian expressed in the so-called laboratory-fixed, center of mass of the nuclei (LF-CMN), frame, whose origin is fixed to the CMN and whose axes remain parallel to those of the LF frame. Furthermore, relativistic and mass-polarization contributions to this Hamiltonian are neglected (Pa68), and the coupling between electronic spin and orbital angular momentum is assumed to be small. In this LF-CMN frame, $\vec{R}$ is the relative position vector of the two nuclei labeled a and b, having masses m_a and m_b , respectively. The N electrons are located by the set of space-spin coordinates $\{\vec{x}_i, i=1, N\} = \vec{X}$, where $\vec{x}_i = (\vec{r}_i, s_i)$, $\vec{r}_i$ locating the spatial position and s_i the spin coordinate (α or β) of the i^{th} electron.

In terms of these variables, the LF-CMN Hamiltonian is expressed as

$$H(\vec{R}, \vec{X}) = -(1/2m) \nabla_R^2 + H_{el}(\vec{R}, \vec{X}) , \quad (1)$$

where $m = m_a m_b / (m_a + m_b)$ is the reduced mass of the nuclei, and

$$H_{el}(\vec{R}, \vec{X}) = -1/2 \sum_{i=1}^N \nabla_{r_i}^2 - \sum_{i=1}^N (Z_a/r_{ia} + Z_b/r_{ib}) + \sum_{i < j} 1/r_{ij} + Z_a Z_b/R \quad (2)$$

is the electronic Hamiltonian. In the usual sense, Z_a , r_{ia} and r_{ij} refer to the charge on nucleus a, the distance between the i^{th} electron and nucleus a, and the distance between the i^{th} and j^{th} electrons, respectively. The expressions are in atomic units, where the unit of energy is the Hartree, the unit of distance the Bohr radius (a_0) and the unit of mass that of the electron.

On the right side of Equation (1) the first term represents the relative kinetic energy of the two nuclei, which are the heavy particles taking part in an atom-atom collision. The terms on the right of Equation (2) represent, in order, the kinetic energy of the electrons, the Coulomb attraction energy of the electrons with the nuclei a and b, the electron-electron Coulomb repulsion energy and the Coulomb repulsion energy between nuclei a and b.

The description of a diatomic system can formally be made in terms of the wave function, $\Psi(\vec{R}, \vec{X})$, for the total system of nuclei and electrons, which satisfies the time independent Schrödinger equation,

$$H(\vec{R}, \vec{X})\Psi(\vec{R}, \vec{X}) = E\Psi(\vec{R}, \vec{X}) \quad , \quad (3)$$

where E is the total energy of the system. In solving Equation (3) it is important to pay attention to the angular momentum of the electrons and nuclei. The total orbital angular momentum, $\vec{K}$, is the sum of the nuclear and electronic orbital angular momenta, $\vec{L}^{(n)}$ and $\vec{L}^{(e)}$, where

$$\vec{L}^{(n)} = -\vec{R} \times i\vec{\nabla}_R \quad (4)$$

and

$$\vec{L}^{(e)} = - \sum_{i=1}^N \vec{r}_i \times i\vec{\nabla}_{r_i} \quad (5)$$

The LF-CMN components, K_x , K_y and K_z , as well as $K^2 = \vec{K} \cdot \vec{K}$, all obey the usual commutation relations for angular momenta, and commute with the LF-CMN Hamiltonian of Equation (1), owing to its rotational invariance. Accordingly, the solution, $\Psi(\vec{R}, \vec{X})$, of Equation (3) is simultaneously an eigenfunction of K^2 and K_z , with eigenvalues $K(K+1)$ and M , respectively, and the total orbital angular momentum and its z component are constants of the motion. Because of the assumption of negligible spin-orbit coupling for the electrons, the spin angular momentum has been left out of this discussion for convenience, but could easily be included. So, with no loss of generality, the solution to Equation (3) is classified according to the constants of the motion, K^2 and K_z , and is written

$$\Psi(\vec{R}, \vec{X}) = \Psi_{KM}(\vec{R}, \vec{X}) \quad (6)$$

2. Remarks Regarding Reference Frames

At this point attention will be turned toward specifically pedagogical considerations, providing a reminder of some basic concepts of a mathematical and physical nature which are helpful in understanding the approach which will be taken in solving Equation (3). The remarks which follow will serve to reiterate some key ideas which have long been established (see, for example, Kr30). The ideas are not easy to grasp, and are often passed over either in too sophisticated or too cursory a way in the literature. Notable exceptions, however, can be found (Kr30, Vl51, Ho62, Th61, Th65, Pa68, Sm69).

As it stands, Equation (3) involves the Hamiltonian and wave function, Ψ_{KM} , expressed as functions of $\vec{R}$ and $\{\vec{r}_i\}$ referred to the LF-CMN frame. The axes of this frame are labeled by x , y and z . The i^{th} electron is thus located by $\vec{r}_i$ having coordinates (x_i, y_i, z_i) . $\vec{R}$ is most conveniently represented by its spherical polar coordinates, R , θ and ϕ . Therefore, in the LF-CMN frame, $(x_i, y_i, z_i, R, \theta, \phi)$ constitute an independent set of coordinates in which to solve Equation (3).

In terms of these coordinates, the components in the LF-CMN frame of $\vec{L}^{(n)}$ and $\vec{L}^{(e)}$ (Equations (4) and (5)) appear as

$$\begin{aligned}
 L_x^{(n)} &= i(\sin\phi\partial/\partial\theta + \cot\theta\cos\phi\partial/\partial\phi) \\
 L_y^{(n)} &= i(-\cos\phi\partial/\partial\theta + \cot\theta\sin\phi\partial/\partial\phi) \\
 L_z^{(n)} &= -i\partial/\partial\phi
 \end{aligned} \tag{7}$$

and

$$\begin{aligned}
 L_x^{(e)} &= -i \sum_{i=1}^N (y_i \partial/\partial z_i - z_i \partial/\partial y_i) \\
 L_y^{(e)} &= -i \sum_{i=1}^N (z_i \partial/\partial x_i - x_i \partial/\partial z_i) \\
 L_z^{(e)} &= -i \sum_{i=1}^N (x_i \partial/\partial y_i - y_i \partial/\partial x_i) .
 \end{aligned} \tag{8}$$

The wave function of Equation (6) can also be written explicitly in terms of these variables to read

$$\Psi_{KM}(\vec{R}, \vec{X}) = \Psi_{KM}(R, \theta, \phi, x_i, y_i, z_i) . \tag{9}$$

Also, the first term on the right of Equation (1), expressing the relative kinetic energy of the nuclei, appears as follows (see, for example, Co62):

$$\begin{aligned}
 -(1/2m) \nabla_R^2 &= -(1/2mR^2) \{ \partial/\partial R (R^2 \partial/\partial R) \\
 &\quad + \cot\theta \partial/\partial\theta + \partial^2/\partial\theta^2 \\
 &\quad + \sin^{-2}\theta \partial^2/\partial\phi^2 \} .
 \end{aligned} \tag{10}$$

One can check that the terms within the brackets of Equation (10), involving the angles, can be replaced by $-\vec{L}^{(n)} \cdot \vec{L}^{(n)}$, according to Equation (7) (see, for example, Ed60). It is important to keep in mind that partial derivatives, such as occur in Equations (7), (8) or (10), depend upon which variables are actually independent of one another during differentiation. Because the LF-CMN frame constitutes an inertial reference frame, the set of variables, $(x_i, y_i, z_i, R, \theta, \phi)$, of the electrons and nuclei is indeed an independent set of variables. Therefore, for example, $\partial/\partial\theta$ in Equation (10) means to differentiate with respect to θ while holding all other variables, (x_i, y_i, z_i, R, ϕ) , fixed. Similar considerations hold in turn for each variable in this set.

Now one would like to proceed to solve Equation (3) by expanding the wave function of Equation (9) in a complete set of electronic wave functions at each $\vec{R}$. It is here that the need arises to express Equation (3) in terms of variables referred to a coordinate frame in which the internuclear vector $\vec{R}$ is fixed. This is due to the fact that normally electronic wave functions are determined in such coordinate frames. Such a reference frame, fixed to the nuclei with origin at the CMN, will be called a body-fixed, CMN (BF-CMN) frame. The key concept regarding electronic wave functions is that they are usually calculated

under conditions where the set of electronic coordinates in the BF-CMN frame are treated as independent variables.

The BF-CMN frame considered here shall have axes x' , y' , z' , where the z' axis is along the internuclear vector $\vec{R}$. Consequently, the angles ϕ and θ are the first two of the Euler angles (see, for example, Ju75) which rotate the SF-CMN frame into the BF-CMN frame. The third Euler angle, γ , can be freely chosen since it only serves to define the x' and y' axes, which can be arbitrarily set for a diatomic molecule (Ju75). Therefore, γ is an auxiliary variable, and as such will play only an indirect role in what follows. Figure 1 shows the Euler angles $(\phi\theta\gamma)$ by which the SF-CMN frame is rotated into the BF-CMN frame.

The coordinates of the internuclear vector in the BF-CMN frame are simply $(R,0,0)$. The i^{th} electron, with coordinates (x_i, y_i, z_i) in the LF-CMN frame, has coordinates (x'_i, y'_i, z'_i) in the BF-CMN frame, specified for a given orientation (θ, ϕ) of the internuclear vector by the unitary transformation (see, for example, Ti64 and Ju75)

$$\begin{aligned} x'_i &= x'_i(\phi\theta\gamma) = (\cos\gamma\cos\theta\cos\phi - \sin\gamma\sin\phi)x_i \\ &\quad + (\cos\gamma\cos\theta\sin\phi + \sin\gamma\cos\phi)y_i - \cos\gamma\sin\theta z_i \\ y'_i &= y'_i(\phi\theta\gamma) = -(\sin\gamma\cos\theta\cos\phi + \cos\gamma\sin\phi)x_i \\ &\quad + (-\sin\gamma\cos\theta\sin\phi + \cos\gamma\cos\phi)y_i + \sin\gamma\sin\theta z_i \end{aligned}$$

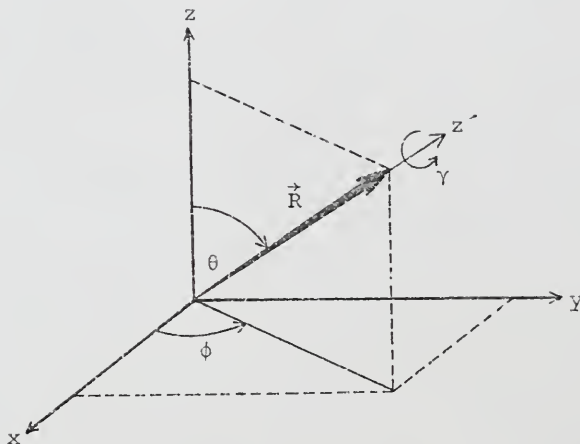


Figure 1. The Euler angles ($\phi\theta\gamma$) relating the SF-CMN frame (x, y, z axes) to the BF-CMN frame (x', y', z' axes). γ specifies the x' and y' axes, which can be arbitrarily chosen and are not shown. $\vec{R}$ labels the internuclear vector.

$$z'_i = z'_i(\phi\theta) = \sin\theta\cos\phi x_i + \sin\theta\sin\phi y_i + \cos\theta z_i . \quad (11)$$

Here attention has been drawn to the dependence of x'_i, y'_i and z'_i on the angles ϕ , θ and γ . The inverse transformation, giving the coordinates (x_i, y_i, z_i) of the i^{th} electron in the SF-CMN frame in terms of its coordinates (x'_i, y'_i, z'_i) in the BF-CMN frame, is,

$$\begin{aligned} x_i &= (\cos\gamma\cos\theta\cos\phi - \sin\gamma\sin\phi)x'_i \\ &\quad - (\sin\gamma\cos\theta\cos\phi + \cos\gamma\sin\phi)y'_i + \sin\theta\cos\phi z'_i \\ y_i &= (\cos\gamma\cos\theta\sin\phi + \sin\gamma\cos\phi)x'_i \\ &\quad + (-\sin\gamma\cos\theta\sin\phi + \cos\gamma\cos\phi)y'_i + \sin\theta\sin\phi z'_i \\ z_i &= -\cos\gamma\sin\theta x'_i + \sin\gamma\sin\theta y'_i + \cos\theta z'_i . \end{aligned} \quad (12)$$

With these expressions, the Schrödinger equation of Equation (3) in the LF-CMN frame, where $(x_i, y_i, z_i, R, \theta, \phi)$ are independent variables, can be rewritten allowing the BF-CMN electronic variables (x'_i, y'_i, z'_i) to be treated as independent variables (as they are in molecular electronic structure calculations). The expression, "treated as independent variables", in the preceding sentence speaks to an important concept. To an observer in the BF-CMN

frame, the electronic and nuclear coordinates are simply $(x'_1, y'_1, z'_1, R, 0, 0)$. But such an observer must keep in mind that the BF-CMN frame is not an inertial frame, and, by Equation (11), (x'_1, y'_1, z'_1) have explicit $(\phi\theta\gamma)$ dependence for a given set of electronic coordinates in the LF-CMN frame.

In order for an observer in the BF-CMN frame to use the electronic variables (x'_1, y'_1, z'_1) as independent variables in treating Equation (3), two new variables, θ' and ϕ' , may be introduced with two restrictions: (1) the set $(x'_1, y'_1, z'_1, R, \theta', \phi')$ must be an independent set of variables for the observer in the BF-CMN frame, and (2) θ' and ϕ' must be given by,

$$\begin{aligned}\theta' &= \theta, \\ \phi' &= \phi.\end{aligned}\tag{13}$$

According to this equation, $(\theta'\phi')$ may seem to be redundant variables, but this is not at all the case. The variables (x'_1, y'_1, z'_1) are independent of $(\theta'\phi')$ as far as the observer in the BF-CMN frame is concerned, and Equation (13) simply specifies their values in terms of variables which are determined by an observer in the LF-CMN (inertial) frame. Equation (13) gives the relationships for θ' and ϕ' just as Equation (11) does for x'_1, y'_1 and z'_1 .

Equation (3) will now be transformed so that an ob-

server in the BF-CMN frame could attempt to solve it in terms of the independent set $(x'_i, y'_i, z'_i, R, \theta', \phi')$. Such a transformation involves both the Hamiltonian operator (see Equations (1), (2) and (10)) as well as the wave function (see Equation (9)). First the Hamiltonian will be considered.

For clarity, when performing partial differentiation involving the independent variables $(x_i, y_i, z_i, R, \theta, \phi)$, the symbol ∂ , which has already been used, will now specifically indicate that, when a variable of differentiation from this set has been singled out, all the others are held fixed. For instance,

$$\partial/\partial\theta \equiv \partial/\partial\theta|_{\{(x_i, y_i, z_i), R, \phi\}} \quad , \quad (14)$$

where the variables held fixed are explicitly indicated. Similarly, ∂' will be used to indicate partial differentiation involving the independent variables $(x'_i, y'_i, z'_i, R, \theta', \phi')$. By analogy with Equation (14) for instance,

$$\partial'/\partial\theta' = \partial'/\partial\theta'|_{\{(x'_i, y'_i, z'_i), R, \phi'\}} \quad . \quad (15)$$

Then, if w is one of the variables $(x_i, y_i, z_i, R, \theta, \phi)$,

$$\partial/\partial w \rightarrow (\partial\theta'/\partial w)\partial'/\partial\theta' + (\partial\phi'/\partial w)\partial'/\partial\phi' + \sum_{i=1}^N \{ (\partial x'_i/\partial w)\partial'/\partial x'_i + (\partial y'_i/\partial w)\partial'/\partial y'_i + (\partial z'_i/\partial w)\partial'/\partial z'_i \}. \quad (16)$$

A similar relation holds for expressing $\partial'/\partial w'$ as a linear combination of partial derivatives involving the variables $(x_i, y_i, z_i, R, \theta, \phi)$ where w' is one of the variables $(x'_i, y'_i, z'_i, R, \theta', \phi')$. These are useful expressions to keep in mind, especially as to their meaning emphasized by using the ∂ and ∂' notation. This conceptual and notational viewpoint follows the work of Kronig (Kr30).

Referring now to Equation (2), the kinetic energy of the i^{th} electron involves the operator,

$$\nabla_{r_i}^2 = \partial^2/\partial x_i^2 + \partial^2/\partial y_i^2 + \partial^2/\partial z_i^2. \quad (17)$$

On the basis of Equations (11) and (16), one can write

$$\begin{aligned} \partial/\partial x_i &\rightarrow (\cos\gamma\cos\theta\cos\phi - \sin\gamma\sin\phi)\partial'/\partial x'_i \\ &- (\sin\gamma\cos\theta\cos\phi + \cos\gamma\sin\phi)\partial'/\partial y'_i + \sin\theta\cos\phi\partial'/\partial z'_i, \end{aligned} \quad (18)$$

with similar expressions for $\partial/\partial y_i$ and $\partial/\partial z_i$. Using these expressions directly, one finds that

$$\begin{aligned} \partial^2/\partial x_i^2 + \partial^2/\partial y_i^2 + \partial^2/\partial z_i^2 + \\ \partial'^2/\partial x_i'^2 + \partial'^2/\partial y_i'^2 + \partial'^2/\partial z_i'^2 = \nabla_{r_i'}^2. \end{aligned} \quad (19)$$

The potential energy terms in Equation (2) involve only the distances between electrons and nuclei, and therefore are unchanged in going from the variables $(x_i, y_i, z_i, R, \theta, \phi)$ to the variables $(x'_i, y'_i, z'_i, R, \theta', \phi')$. Consequently, the electronic Hamiltonian of Equation (2) takes the same form for an observer in the BF-CMN frame as for an observer in the LF-CMN frame.

Such is not the case for the first term of Equation (1), which is expressed in the variables (R, θ, ϕ) in Equation (10). By a straightforward, but tedious, application of Equation (16), using Equations (11) and (12), one finds that

$$\partial/\partial\theta \rightarrow \partial'/\partial\theta' - i\cos\gamma L_{Y'}^{(e)} - i\sin\gamma L_{X'}^{(e)} \quad (20)$$

and

$$\partial/\partial\phi \rightarrow \partial'/\partial\phi' - i\cos\theta' L_{Z'}^{(e)} + i\sin\theta' (\cos\gamma L_{X'}^{(e)} - \sin\gamma L_{Y'}^{(e)}) . \quad (21)$$

Here, $L_{X'}^{(e)}$, $L_{Y'}^{(e)}$ and $L_{Z'}^{(e)}$ are the components of the electronic orbital angular momentum in the BF-CMN frame. They are expressed according to Equation (8) by replacing all LF-CMN quantities by their appropriate BF-CMN (primed) counterparts. Equations (20) and (21), again with some tedious algebra, lead to the following result for the angular terms in Equation (10):

$$\begin{aligned}
 & \cot\theta \partial/\partial\theta + \partial^2/\partial\theta^2 + \sin^{-2}\theta \partial^2/\partial\phi^2 \rightarrow \\
 & \rightarrow \cot\theta' \partial'/\partial\theta' + \partial'^2/\partial\theta'^2 + \sin^{-2}\theta' \partial'^2/\partial\phi'^2 \\
 & - i(e^{-i\gamma_{L_+}(e)} + e^{i\gamma_{L_-}(e)}) \partial'/\partial\theta' - (L^{(e)}_{\pm})^2 \\
 & - 2i(\cot\theta/\sin\theta) \partial'/\partial\phi' L^{(e)}_{z'} - \cot^2\theta (L^{(e)}_{z'})^2 + (L^{(e)}_{z'})^2 \\
 & - (2/\sin\theta)(\cos\gamma_{L^{(e)}_{x'}} - \sin\gamma_{L^{(e)}_{y'}})(i\partial'/\partial\phi' - \cos\theta L^{(e)}_{z'}) \quad (22)
 \end{aligned}$$

Here, in the usual way, $L_{\pm}^{(e)} = L_{x'}^{(e)} \pm iL_{y'}^{(e)}$. The R dependent terms in Equation (10) are unaffected in the transformation from the LF-CMN frame to the BF-CMN frame. Consequently, replacing the angular terms of Equation (10) by the right side of Equation (22) leads to the appropriate Hamiltonian operator (see Equation (1)) which can be used by an observer in the BF-CMN frame in order to formally treat the behavior of the electrons and nuclei.

The first three terms on the right side of Equation (22) are similar to those found in the LF-CMN Hamiltonian. The remaining terms are those compensating for Coriolis effects due to the fact that the BF-CMN frame is not an inertial frame. In a sense, the inclusion of these Corolis terms is the price paid by the BF-CMN observer in order to reckon $(x'_i, y'_i, z'_i, R, \theta', \phi')$ as independent variables.

3. Remarks Regarding the Wave Function

The wave function of the total system of electrons and nuclei (see Equation (9)) must also be properly transformed and expressed in terms of appropriate functions in the BF-CMN frame. Here the approach of Davydov (Da65) is adopted.

Attention is drawn again to the fact that the wave function of Equation (9) is an eigenfunction of the square of the total orbital angular momentum, K^2 , and its component along the LF-CMN Z axis, K_z , with eigenvalues $K(K+1)$ and M , respectively. Following Davydov (Da65), if a coordinate frame undergoes a transformation by rotation through Euler angles $(\alpha\beta\gamma)$ to another coordinate frame, then an eigenfunction in the first frame of K^2 and K_z , with eigenvalues, respectively, $K(K+1)$ and M , can be written as a linear combination of the $(2K+1)$ such eigenfunctions in the rotated frame, all of which are eigenfunctions of K^2 with eigenvalue $K(K+1)$, and each of which is an eigenfunction of K_z with eigenvalue, Λ , among the possible values $K, K-1, \dots, -K$.

For the case considered here, of a transformation from the LF-CMN frame to the BF-CMN frame through Euler angles $(\phi\theta\gamma)$, the wave function of Equation (9) can be written

$$\Psi_{KM}(R, \theta, \phi, x_i, y_i, z_i) = \sum_{\Lambda=-K}^K D_{M, \Lambda}^K(\phi\theta\gamma) \Psi_{K\Lambda}^M(R, 0, 0, x'_i, y'_i, z'_i) . \quad (23)$$

Here the expansion coefficients, $D_{M,\Lambda}^K(\phi\theta\gamma)$, are the so-called generalized spherical functions, or D-functions, and are eigenfunctions of the symmetric top. A good discussion of their properties is given by Edmonds (Ed60). In Equation (23), $\Psi_{K\Lambda}^M(R, 0, 0, x'_i, y'_i, z'_i)$ is an eigenfunction of K_Z , the component of $\vec{K}$ along the internuclear axis, with eigenvalue Λ . The orbital angular momentum of the nuclei has no component along the internuclear axis, as can easily be verified from Equation (4). As a consequence, $K_Z = L_Z^{(e)}$.

It is at this point that it is convenient to introduce a complete set of electronic wave functions at each internuclear separation, R . The electronic wave functions employed can be any of the ones commonly calculated, where the electronic variables, (x'_i, y'_i, z'_i) , in the BF-CMN frame are taken as an independent set of variables. Such electronic wave functions, whether of the single-configuration or more elaborate configuration-interaction type, are classified according to their component of electronic orbital angular momentum along the internuclear axis. That is, they are constructed as eigenfunctions of $L_Z^{(e)}$ having eigenvalues denoted by Λ . For each Λ , the complete set of electronic wave functions, $\{\Phi_{n\Lambda}(R, x'_i, y'_i, z'_i)\}$, will be introduced at each R , and will be taken to be orthonormal. Then each $\Psi_{K\Lambda}^M(R, 0, 0, x'_i, y'_i, z'_i)$ of Equation (23) may be expanded in the set of electronic wave functions, $\{\Phi_{n\Lambda}\}$:

$$\psi_{K\Lambda}^M(R, 0, 0, x'_1, y'_1, z'_1) = \sum_n \{ \psi_{n\Lambda}^{KM}(R)/R \} \phi_{n\Lambda}(R, x'_1, y'_1, z'_1) . \quad (24)$$

Substitution of Equation (24) into Equation (23) gives a useful expansion for the total wave function of nuclei and electrons in terms of functions of the electronic variables (x'_1, y'_1, z'_1) in the BF-CMN frame:

$$\Psi_{KM}(R, \theta, \phi, x_1, y_1, z_1) = (1/R) \sum_{\Lambda} \sum_n \psi_{n\Lambda}^{KM}(R) D_{M, \Lambda}^K(\phi \theta \gamma) \phi_{n\Lambda}(R, x'_1, y'_1, z'_1) . \quad (25)$$

It should be emphasized that the equal sign in Equations (23) and (25) means equality only in the sense that in each case the function on the left of the expression, where the variables are the coordinates of the electrons and nuclei in the LF-CMN frame, can be replaced by the linear combination of functions on the right of the expression, where the variables are the coordinates of the electrons and nuclei in the BF-CMN frame. The presence of the variables ϕ and θ in the D-functions on the right of Equations (23) and (25) will be discussed presently.

4. The Coupled Equations and Coulomb and Born-Oppenheimer Couplings

Recalling the previous discussion regarding the Hamiltonian operator, Equations (19) and (22) provide an observer in the BF-CMN frame the appropriate Hamiltonian for

the nuclei and electrons under conditions where $(x'_1, y'_1, z'_1, R, \theta', \phi')$ are independent variables. Using this Hamiltonian, an observer in the BF-CMN frame may now replace ϕ and θ on the right hand side of Equation (25) by ϕ' and θ' according to Equation (13). Then the right side of Equation (25) becomes an appropriate expansion for the "transformed" wave function, $\tilde{\Psi}_{KM}(R, \theta', \phi', x'_1, y'_1, z'_1)$, which satisfies the "transformed" Schrödinger equation. Thus, an observer in the BF-CMN frame may proceed to solve Equation (3) by relying on Equations (19) and (22) and solving for the wave function

$$\tilde{\Psi}_{KM}(R, \theta', \phi', x'_1, y'_1, z'_1) = (1/R) \sum_{\Lambda} \sum_n \Psi_{n\Lambda}^{KM}(R) D_{M,\Lambda}^K(\phi' \theta' \gamma) \Phi_{n\Lambda}(R, x'_1, y'_1, z'_1). \quad (26)$$

In dealing with the operators in Equation (22), it will be useful to rely on some of the formal properties of the D-functions (Ed60). The D-functions, $D_{M,\Lambda}^K(\phi \theta \gamma)$ are formally associated with rotations through the Euler angles $\{\phi \theta \gamma\}$, and these rotations are generated by the angular momentum operator, $\vec{N}$, whose components are

$$\begin{aligned} N_x(\phi \theta \gamma) &= L_x^{(n)} - i(\cos \phi / \sin \theta) \partial / \partial \gamma, \\ N_y(\phi \theta \gamma) &= L_y^{(n)} - i(\sin \phi / \sin \theta) \partial / \partial \gamma, \\ N_z(\phi \theta \gamma) &= L_z^{(n)}, \end{aligned} \quad (27)$$

where $L_X^{(n)}$, $L_Y^{(n)}$ and $L_Z^{(n)}$ are given in Equation (7). The D-functions are eigenfunctions of $N^2 = N_X^2 + N_Y^2 + N_Z^2$:

$$N^2(\phi\theta\gamma)D_{M,\Lambda}^K(\phi\theta\gamma) = K(K+1)D_{M,\Lambda}^K(\phi\theta\gamma). \quad (28)$$

By expanding out $N^2(\phi\theta\gamma)$ using Equation (27), and recalling that the ϕ and γ dependence of $D_{M,\Lambda}^K(\phi\theta\gamma)$ is in the factors $e^{iM\phi}$ and $e^{i\Lambda\gamma}$, Equation (28) can be rearranged as follows (Ed60):

$$\begin{aligned} & (\partial^2/\partial\theta^2 + \cot\theta\partial/\partial\theta + \sin^{-2}\theta\partial^2/\partial\phi^2)D_{M,\Lambda}^K(\phi\theta\gamma) \\ & = \{\sin^{-2}\theta(\Lambda^2 - 2\cos\theta M\Lambda) - K(K+1)\}D_{M,\Lambda}^K(\phi\theta\gamma). \end{aligned} \quad (29)$$

Other useful relationships involve the operators $N_{\pm}(\phi\theta\gamma) = N_X \pm iN_Y$. In particular, based on the properties of the D-functions (Ed60), it can be shown that

$$N_{\pm}(\phi\theta\gamma)D_{M,\Lambda}^K(\phi\theta\gamma) = -\lambda_{\pm}D_{M,\Lambda\pm 1}^K(\phi\theta\gamma) \quad (30)$$

where $\lambda_{\pm} = \{K(K+1) - \Lambda(\Lambda\pm 1)\}^{1/2}$. Furthermore, $\partial/\partial\theta$ can be expressed as

$$\partial/\partial\theta = \frac{1}{2}(e^{-i\phi}N_+ - e^{i\phi}N_-) \quad (31)$$

Using Equations (19), (22) and (31), the BF-CMN Hamiltonian can be expressed as follows:

$$\begin{aligned} \tilde{H}(R, \theta', \phi', x_1', y_1', z_1') &= -(1/2mR^2)\partial/\partial R(R^2\partial/\partial R) \\ &- (1/2mR^2)\{\cot\theta'\partial'/\partial\theta' + \partial'^2/\partial\theta'^2 + \sin^{-2}\theta'\partial'^2/\partial\phi'^2 \end{aligned}$$

$$\begin{aligned}
 & - \frac{1}{2}i(e^{-i\gamma_{L_+}(e)} + e^{i\gamma_{L_-}(e)}) (e^{-i\phi' N_+ (\phi' \theta' \gamma)} - e^{i\phi' N_- (\phi' \theta' \gamma)}) \\
 & - (L^{(e)})^2 - 2i(\cot \theta' / \sin \theta') \partial' / \partial \phi' L_z^{(e)} - \cot^2 \theta' (L_z^{(e)})^2 + (L_z^{(e)})^2 \\
 & - (1/\sin \theta') (e^{i\gamma_{L_+}(e)} + e^{-i\gamma_{L_-}(e)}) \{i \partial' / \partial \phi' - \cos \theta' L_z^{(e)}\} \\
 & + H_{el}(R, x_i', y_i', z_i') \quad . \quad (32)
 \end{aligned}$$

Now, in the usual way, the right side of Equation (26) may be substituted into the "transformed" Schrödinger equation,

$$(\tilde{H} - E) \tilde{\Psi}_{KM} = 0 \quad . \quad (33)$$

When this is done, many of the terms from the operators of Equation (32) acting on functions $D_{M,\Lambda}^K \phi_{n\Lambda}$ of Equation (26) will combine and lead to simplifications. One can, for example, compare the contributions from some of the operators involving $L_z^{(e)}$ in Equation (32) with the terms involving Λ on the right side of Equation (29).

Upon multiplication of Equation (33) on the left by $D_{M,\Lambda}^{K*} (\phi' \theta' \gamma) \phi_{n\Lambda}^* (R, x_i', y_i', z_i')$, followed by integration over the coordinates $(\phi', \theta', \gamma, x_i', y_i', z_i')$, the following set of coupled equations for the radial functions $\psi_{n\Lambda}^{KM}(R)$ results:

$$\begin{aligned}
 & \{-(1/2m) d^2/dR^2 - (1/2mR^2) [2\Lambda^2 - K(K+1)] - E\} \psi_{n\Lambda}^{KM}(R) \\
 & = \sum_{n'\Lambda'} \{ \langle \phi_{n\Lambda} | H_{el} | \phi_{n'\Lambda'} \rangle - (1/2mR^2) \langle \phi_{n\Lambda} | (L^{(e)})^2 | \phi_{n'\Lambda'} \rangle \\
 & + (1/m) \langle \phi_{n\Lambda} | d/dR | \phi_{n'\Lambda'} \rangle + (1/2m) \langle \phi_{n\Lambda} | d^2/dR^2 | \phi_{n'\Lambda'} \rangle \} \delta_{\Lambda,\Lambda'}
 \end{aligned}$$

$$\begin{aligned}
 & - (1/2\pi R^2) \langle \Phi_{n\Lambda} | L_+^{(e)} | \Phi_{n'\Lambda'} \rangle g_{\Lambda\Lambda'}^{KM+} \delta_{\Lambda, \Lambda'+1} \\
 & - (1/2\pi R^2) \langle \Phi_{n\Lambda} | L_-^{(e)} | \Phi_{n'\Lambda'} \rangle g_{\Lambda\Lambda'}^{KM-} \delta_{\Lambda, \Lambda'-1} \rangle \psi_{n'\Lambda'}^{KM}(R) \quad . \quad (34)
 \end{aligned}$$

Here, the brackets indicate integration over electronic variables. The coefficients $g_{\Lambda\Lambda'}^{KM\pm}$ are given by

$$g_{\Lambda\Lambda'}^{KM\pm} = (2K+1)(8\pi^2)^{-1} \int d\phi' \sin\theta' d\theta' d\gamma D_{M,\Lambda}^{K*}(\phi'\theta'\gamma) G_{M,\Lambda'}^{K\pm}(\phi'\theta'\gamma) \quad , \quad (35)$$

where

$$\begin{aligned}
 G_{M\Lambda}^{K\pm}(\phi'\theta'\gamma) &= e^{\pm i\gamma} (M \sin^{-1}\theta' + \Lambda \cot\theta') D_{M\Lambda}^K(\phi'\theta'\gamma) \\
 &+ (i/2) e^{\mp i\gamma} \{ \lambda_+ e^{-i\phi'} D_{M,\Lambda+1}^K(\phi'\theta'\gamma) - \lambda_- e^{i\phi'} D_{M,\Lambda-1}^K(\phi'\theta'\gamma) \} \quad . \quad (36)
 \end{aligned}$$

In Equation (34), all of the various couplings between the nuclear and electronic motions are included explicitly. The radial Born-Oppenheimer couplings appear in the matrix elements between the electronic expansion states over the d/dR and d^2/dR^2 operators, and reflect the effect of the radial motion of the nuclei on the electronic motion. As can be seen, radial Born-Oppenheimer couplings exist only between electronic states having the same value of Λ . The rotational Born-Oppenheimer couplings appear in the matrix elements over the $L_{\pm}^{(e)}$ and $(L^{(e)})^2$ operators, and reflect the effect of the rotational motion of the nuclei on the electronic motion. A convenience of treating the problem in the BF-CMN frame is that the influence of nuclear rotational motion on the behavior of the electrons becomes expressed in terms of matrix elements between elec-

tronic states over electronic angular momentum operators, rather than nuclear angular momentum operators. As can be seen, rotational coupling due to $L_{\pm}^{(e)}$ exists only between electronic states having Λ values differing from one another by ± 1 , whereas coupling due to $(L^{(e)})^2$ exists between electronic states having the same Λ value. The so-called Coulomb coupling appears in the matrix element over the electronic Hamiltonian in Equation (34), and exists only between electronic states having the same value of Λ .

5. Discussion

Some brief remarks are in order regarding the considerations of this chapter. No qualifications have been placed on the basis set of electronic wave functions, $\{\phi_{n\Lambda}\}$, used in the expansion of Equation (26), other than that it be complete and orthonormal. Traditionally, approaches to molecular electronic structure have tended to focus on electronic states which are eigenfunctions of the electronic Hamiltonian, H_{el} , and which therefore leave the matrix of H_{el} diagonal. These are the so-called adiabatic states which provide an adiabatic representation. In such a representation all of the coupling between the electronic states, associated with inelastic collisional processes, rests in the Born-Oppenheimer terms of Equation (34). The eigenenergies of H_{el} associated with these adiabatic states

obey the non-crossing rule, as is well known.

However, in treating atomic and molecular collision processes, it is not at all clear that the set of adiabatic states is always the most appropriate representation to use. Stemming from the point of view emphasized by Lichten (Li63), much consideration and discussion have resulted regarding the importance of the so-called diabatic representations. These representations are comprised of electronic states which are not eigenfunctions of H_{el} . Consequently, the diagonal matrix elements of these states with H_{el} need not obey the non-crossing rule, and the off-diagonal matrix elements may be appreciable. Compared to the Born-Oppenheimer couplings, the Coulomb couplings in a diabatic representation can often actually be the dominant source of coupling associated with inelastic processes influencing the heavy particle motion described by the coupled equations of Equation (34).

Two particularly good discussions of these matters have been made by Smith (Sm69) and Sidis (Si76). Here, it is simply pointed out that the appropriateness of the adiabatic or a particular diabatic representation depends upon how successfully the dominant coupling terms can be identified, as well as calculated or estimated. Radial Born-Oppenheimer couplings are difficult to calculate and normally must be estimated. In addition, they are character-

ized by singularities in regions of R near avoided crossings of the associated adiabatic eigenenergies. The coupling through H_{el} of diabatic states can be estimated, if not often calculated. However, because of frequent lack of information about the Born-Oppenheimer couplings, one cannot always be sure when the Coulomb couplings constitute the dominant contribution in describing inelastic processes. As can be seen from Equation (34), the rotational Born-Oppenheimer couplings have a R^{-2} dependence. Therefore, their contribution will be of increasing importance as distances of closest approach of the nuclei become smaller.

The research related to atomic collision processes reported in the remainder of this dissertation has been carried out within the framework of diabatic representations. In this connection, electronic states constructed as determinants of one-electron molecular orbitals are particularly useful. Furthermore, the behavior of the one-electron molecular orbitals and associated orbital energies can itself provide information of use regarding inelastic processes in atom-atom collisions. Considerations along these lines are pursued in Chapter II, illustrated by molecular orbital calculations on some rare gas diatomic molecules, and in Chapter III, where Penning and associative ionization processes in thermal energy collisions of excited (metastable) rare gas atoms with ground state atoms are discussed in terms of

molecular orbital correlation diagrams. An assessment of the angular momentum contributions in the EF-CMN frame of the emitted electron in these processes is made based on the correlation diagrams analyzed in their united atoms limit. In this united atoms analysis the significance of rotational Born-Oppenheimer couplings will need to be considered, as has just been mentioned.

The topic of study in the final chapter is the dynamics involved in Penning ionization of Argon by metastable Helium in thermal energy collisions. The approach will be to solve numerically in a two state approximation the coupled equations of Equation (34). An interesting feature of chemi-ionization is that the electronic state prior to ionization is embedded in the continuum of electronic states associated with the ionized electron. Thus, in the expansion of Equation (26), the sum over discrete electronic states must be augmented by an integral over the continuum electronic states. This feature will be dealt with in Chapter IV. The solution of the coupled equations with the appropriate boundary conditions for scattering will lead to results for total and partial cross sections for Penning ionization.

CHAPTER II

A STUDY OF SINGLE-ELECTRON AND TOTAL ENERGIES FOR SOME PAIRS OF NOBLE GAS ATOMS

In this chapter* consideration will be given to atom-atom interaction potentials and electronic structure pertinent to the description of collision events. Several features should characterize the method employed in this type of treatment of the electronic structure of atom pairs:

- (a) The method should provide a description of the interaction potentials for the ground as well as excited states which govern the motions of the heavy particles (nuclei) during collisions.
- (b) Details of the electronic structure, at least of the type found within the self-consistent molecular orbital (MO) framework, should be available so that processes related to electronic excitations may be studied, especially in the case of energetic atom-atom collisions.

*This chapter is an essentially unaltered version of a contribution (Be74a) to the Proceedings of the International Symposium on Atomic, Molecular and Solid State Theory and Quantum Statistics held at Sanibel Island, Florida, 20-26 January 1974, where a preliminary report of the results was made.

- (c) The method should be applicable to a variety of pairs of atomic neutral and ionic species while at the same time it should involve only a moderate degree of calculational effort and complexity.

Statistical approaches, such as the Thomas-Fermi-Dirac method, have provided useful results by applying free-electron gas energy expressions in conjunction with a molecular charge density taken as a superposition of atomic charge densities. However, these approaches are deficient in that they only describe the ground state interaction. They afford no information of the type mentioned in point (b), and furthermore they are not applicable to situations where appreciable charge rearrangement occurs in the diatom, since there is usually no provision for self-consistency in the calculations.

These considerations have led to the use of the MSX α method (Jo66, Jo73, Sl71a, Sl71b, Sl72) in this work. It parallels the Hartree-Fock approach in that it provides a one-electron description with corresponding one-electron eigenvalue equations and eigenstates which are solved self-consistently. The method makes use of a convenient local approximation to the exchange potential. Although approximate, the treatment of exchange in the X α approach should be quite adequate in handling the short range part

of atom-atom interactions, where Coulomb and exchange forces between the electrons are the important ones.

The calculational procedure is furthermore based on the "muffin-tin" approximation to the one-electron potential, which entails no additional computational complications as the number of electrons being treated increases. Thus the scheme has wide applicability.

The first application of the $MSX\alpha$ method to interaction potentials of rare gas pairs was a calculation on the Ne-Ne system (Ko72, see also Tr73). In this chapter, calculations performed on the atom pairs, He-He, He-Ar and Ar-Ar are presented, and their relevance to collision phenomena is pointed out. At the outset, aspects of the $X\alpha$ theory and computational approach which directly relate to the present work are described, and limitations of the theory are considered. Results of the calculations are then presented, and finally, a discussion of the results and their significance is given.

1. Theoretical and Computational Considerations

Within the $X\alpha$ formalism (Sl71a, Sl72), the total energy $E_{X\alpha}$, of a system of N electrons is specified by a set of spin-orbitals, $\{n_i\}$, according to the expression

$$E_{X\alpha} = \sum_i n_i \int d\vec{r}_1 u_i^*(\vec{r}_1) \{ -\nabla_1^2 + \sum_a (-2Z_a/r_{1a}) \} u_i(\vec{r}_1)$$

$$\begin{aligned}
 & + \frac{1}{2} \int d\vec{r}_1 \int d\vec{r}_2 \{ 2\rho(\vec{r}_1) \rho(\vec{r}_2) \} / r_{12} \\
 & + \frac{1}{2} \int d\vec{r}_1 \{ \rho^\uparrow(\vec{r}_1) U_{X\alpha}^\uparrow(\vec{r}_1) + \rho^\downarrow(\vec{r}_1) U_{X\alpha}^\downarrow(\vec{r}_1) \} \\
 & + \sum_{a < b} 2Z_a Z_b / R_{ab} \quad . \quad (37)
 \end{aligned}$$

Equation (37) is expressed in Rydberg units, and in the usual sense, Z_a , R_{ab} , r_{1a} , and r_{12} refer to the charge on nucleus a, the distance between nuclei a and b, the distance between $\vec{r}_1$ and the position of nucleus a and the distance between $\vec{r}_1$ and $\vec{r}_2$, respectively. The electronic charge density is

$$\begin{aligned}
 \rho(\vec{r}_1) &= \rho^\uparrow(\vec{r}_1) + \rho^\downarrow(\vec{r}_1) \\
 &= \sum_{i\uparrow} n_i u_i^*(\vec{r}_1) u_i(\vec{r}_1) + \sum_{i\downarrow} n_i u_i^*(\vec{r}_1) u_i(\vec{r}_1) \quad , \quad (38)
 \end{aligned}$$

comprised of the charge density of electrons with spin-up (denoted by $\uparrow$) and that of electrons with spin-down (denoted by $\downarrow$), and

$$U_{X\alpha}^{\uparrow, \downarrow}(\vec{r}_1) = -9\alpha \{ (3/4\pi) \rho^{\uparrow, \downarrow}(\vec{r}_1) \}^{1/3} \quad (39)$$

is the $X\alpha$ local exchange energy density, α being a multiplicative factor. It should be emphasized that $E_{X\alpha}$ is an energy functional depending on the spin-orbitals, u_i , and the occupation numbers, n_i , and does not necessarily rep-

represent an average value of a many-electron wave function over a Hamiltonian operator, as is the case in Hartree-Fock theory.

For a given assignment of the n_i 's, the u_i 's are determined by making $E_{X\alpha}$ stationary with respect to their variation. This leads to a set of eigenvalue equations for the spin-orbitals. For the u_i 's of spin-up, one has

$$\{f_1(\vec{r}_1) + \int d\vec{r}_2 \{2\rho(\vec{r}_2)/r_{12}\} + v_{X\alpha}^\uparrow(\vec{r}_1)\} u_i(\vec{r}_1) = \epsilon_i u_i(\vec{r}_1) \quad , \quad (40)$$

where

$$f_1(\vec{r}_1) = -\nabla_1^2 + \sum_a (-2Z_a/r_{1a}) \quad , \quad (41)$$

and

$$v_{X\alpha}^\uparrow(\vec{r}_1) = 2/3 u_{X\alpha}^\uparrow(\vec{r}_1) \quad . \quad (42)$$

A similar set of equations is obtained for the u_i 's of spin-down. As is well known (S171a, S172), the interpretation of the $X\alpha$ orbital eigenenergies, ϵ_i , differs from that of Hartree-Fock orbital eigenenergies, and is based on the relation,

$$\epsilon_i = \partial E_{X\alpha} / \partial n_i \quad . \quad (43)$$

This condition between $E_{X\alpha}$, the ϵ_i 's and the n_i 's insures that Fermi statistics holds within the framework of the $X\alpha$ description of a system of electrons; namely, the lowest value of $E_{X\alpha}$ for a system of electrons is achieved

when the spin-orbitals of lowest eigenenergies are occupied. Concentrating on diatomics at fixed internuclear distance, R , a state of the electronic system may be identified by means of an assignment of the n_i 's. A convenient way, then, of determining over which region of R a particular N -electron state is the one of lowest energy is by looking at the behavior of the ϵ_i 's for the occupied and unoccupied orbitals of that state, and observing over which region of R the ϵ_i 's of the occupied orbitals are the lowest ones. In the results which follow, this feature will be demonstrated. Equation (43) is also the basis for the familiar transition state approach (Sl71b), from which good approximations may be found to ionization energies as well as excitation energies between electronic states.

In practice Equation (40) is solved by the Multiple Scattering (MS) method (Jo66, Jo73), with the potential operator

$$V(\vec{r}_1) = \int d\vec{r}_2 \{ 2\rho(\vec{r}_2)/r_{12} \} + V_{X\alpha}^\dagger(\vec{r}_1) = V_C(\vec{r}_1) + V_{X\alpha}^\dagger(\vec{r}_1) \quad (44)$$

approximated by a "muffin-tin" form, whereby it is averaged over angles within non-overlapping spherical regions centered on the various nuclear sites and also other sites in the molecule (outer sphere, empty spheres, etc.), and volume-averaged elsewhere. The u_i 's are de-

terminated self-consistently in terms of partial wave expansions within the spherical regions, and expansions in "multiply-scattered" waves elsewhere. Furthermore, at each iteration of the self-consistent procedure, the "muffin-tin" form of $\rho(\vec{r})$, as found from the u_i 's according to Equation (38), is used to evaluate the "muffin-tin" potential as well as the "muffin-tin" approximation to $E_{X\alpha}$ of Equation (37). The reader is referred elsewhere (Co72) for the details about these approximations as well as ways of correcting for them (Da73, Da74a, Da74b). It suffices here to say only that the effect of the "muffin-tin" approximation in the MSX α evaluation of $E_{X\alpha}$ is appreciable. However, orbital energies ϵ_i for diatoms appear to be more reliable than $E_{X\alpha}$ within the MSX α approach (We73).

It has been shown (Sl74) that in obtaining the exchange potential of Equation (42), one need not assume that the electrons of an atom or molecule behave locally like those of a free-electron gas of the same density. Rather, one may assume a spherically symmetric "Fermi hole" and apply dimensional arguments. Nevertheless, considerable discussion has been devoted to shortcomings of exchange potentials of the type in Equation (42) associated with the finite numbers and inhomogeneous spatial distribution of electrons in atomic and molecular systems (Li70, Li71, Li72, Li74, Ra73, Ra75). By means of a more careful

look at the exchange energy of a free-electron gas of a finite number of electrons in a finite volume, corrections to the exchange potential have been derived by separating out the contribution from the interaction of each electron with itself (Li70, Ra73, Ra75); for a small number (≤ 200) of electrons the contribution from this "self-interaction" becomes quite sizable. Estimates of the "self-interaction", based on the above-mentioned corrections, show that in atoms and molecules only about 85% of its contribution to the exchange potential is included in $V_{X\alpha}^{\uparrow}$ (Li72), while the Coulomb potential, V_C , in Equation (44) includes all the "self-interaction". This imbalance may be partially remedied by an adequate choice of the α factor.

Now, a variety of ways have been suggested for specifying the α factor of Equation (39) for a system of electrons (Sc72 and references therein). The values of α for atoms, resulting from the various schemes, almost all display the same trend; namely, for atoms of larger numbers of electrons the values of α tend toward $2/3$, the factor appearing for a free-electron gas, whereas for atoms with few electrons, larger values of α result. Since the "self-interaction" contribution is large for few electrons, this trend in α values has often been interpreted as reflecting the required greater compensation for the deficit in "self-interaction" in the case of few electrons, the compensation

becoming less as more electrons are involved (Li72). Thus, despite the importance of the corrections which have just been reviewed, the $X\alpha$ exchange potential represents quite well the exchange interaction in a system of electrons. As long as the "muffin-tin" approximations are being made, a treatment in terms of the $X\alpha$ exchange potential alone, with a commonly used value of α , is expected to be adequate for describing the short-range interaction between atoms, as mentioned at the beginning of this chapter.

The calculations performed here employed a double precision (14 hexadecimal or roughly 16 decimal digits available per number on an IBM-370/165 computer) version of the $MSX\alpha$ program, MUSCATEL. This precision was required since the interaction energy, ΔE , is computed as the difference between the total energy of the diatom (in our case, $E_{X\alpha}$ in the "muffin-tin" approximation) and that of the two isolated atoms. For instance, the case of Ar-Ar at moderately large internuclear separations, R , involves interaction energies seven orders of magnitude smaller than the total energies used to determine the interaction, hence requiring at least eight significant figures in the total energies. The total energies of the isolated atoms were calculated using the Hartree-Fock-Slater (HFS) atomic program (He63, Za66).

For the homonuclear cases, He-He and Ar-Ar, the so-

called "virial theorem" values of α for the atoms, as reported by Schwarz (Sc72), were used in all regions of the molecules. For He-Ar the respective atomic "virial theorem" values were used in the spherical regions about the atoms, and a weighted mean (weighted according to the number of electrons of each atom) of the two values was used elsewhere. The heteronuclear case of He-Ar required a choice of the radii to be used for the spherical regions about the atomic sites. Contiguous spherical regions were chosen in all cases, and the ratio between the He and Ar sphere radii, used at all internuclear separations calculated, were determined in the following way. Average radii $\langle r \rangle$ obtained from numerical atomic Hartree-Fock calculations (Ma67a, Ma68) were used to estimate the size of each of the isolated closed shell atoms, He and Ar, based on the 1s orbital of He, and the 3p orbital of Ar. The values are, respectively, $0.92727 a_0$ and $1.66296 a_0$. The He and Ar sphere radii at different R were then chosen in the ratio of these two characteristic charge extents. From the same atomic calculations, the maximum values of the He 1s and Ar 3p radial probabilities occur, respectively, at about $0.55 a_0$ and $1.30 a_0$, so for internuclear separations larger than about $1.85 a_0$, the above scheme for selecting sphere sizes should serve well. Other considerations must be made for cases which do not involve two closed shell atoms and where significant charge rear-

rangement occurs in the diatom. Such a case is treated in the following chapter where calculations are reported on the excited He-Ar diatom which separates at large R to $\text{He}^*(1s2s, {}^1, {}^3S)$ plus $\text{Ar}(3p^6, {}^1S)$.

The selection of partial waves to be included in the expansion of an orbital in the various regions depends upon over which regions of the molecule the orbital tends to be concentrated. For a very deep lying core orbital, which is essentially of atomic character, only the partial wave corresponding to that of the associated atomic orbital was used in each appropriate atomic region, since partial waves of other l values give a negligible contribution. For higher lying orbitals, appreciable contribution from a number of partial waves, s , p , d , etc. may occur. Such partial waves were included as long as their amplitudes were at least one-hundredth the amplitude of the dominant partial wave.

All of the calculations required no more than medium size core on an IBM-370/165 computer and the times per iteration of the SCF procedure were about two seconds for He-He, five seconds for He-Ar and between five and ten seconds for Ar-Ar, depending on the "goodness" of the starting point for a calculation. Denoting the absolute difference, occurring between the values of the "muffintin" potential of Equation (44) at one iteration and those

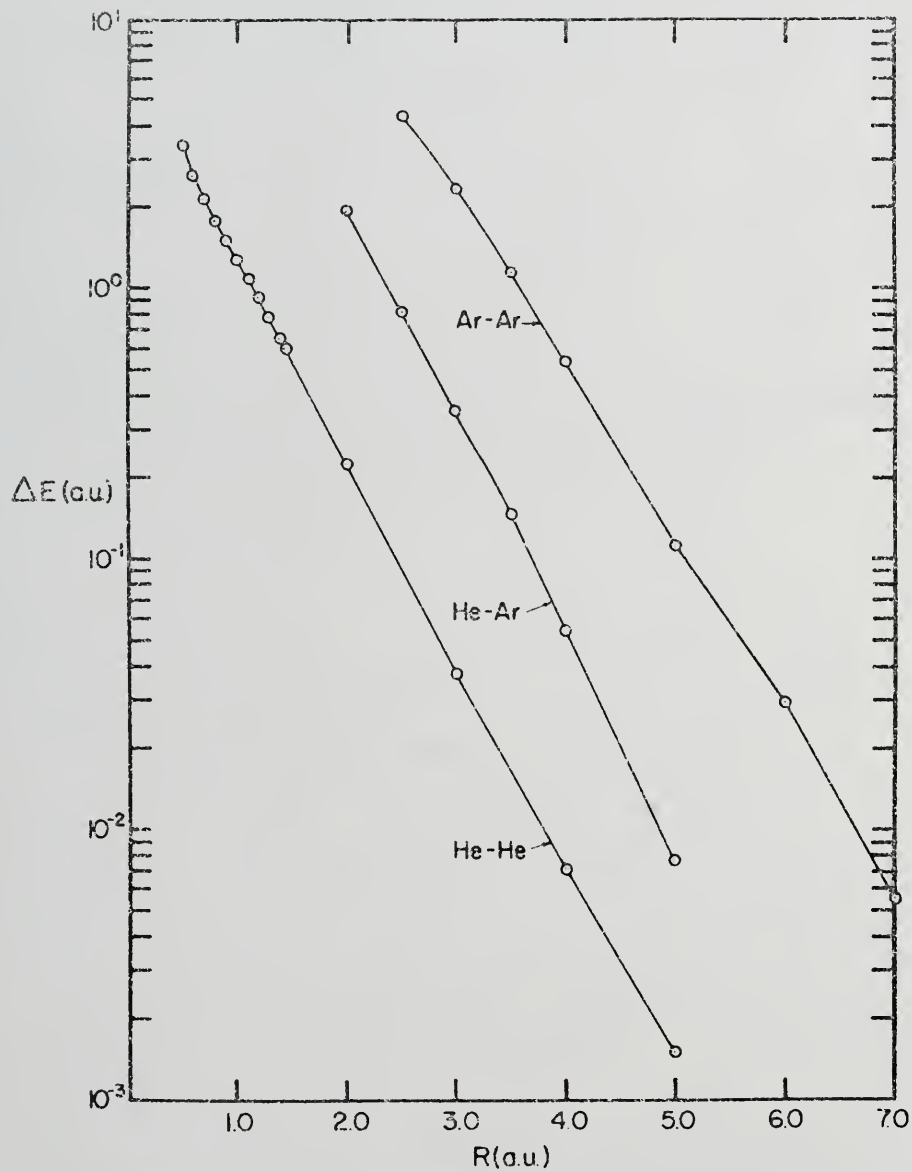
of the previous iteration, by ΔV , and the maximum value of $\Delta V/V$ by ϵ , the degree of self-consistency $\epsilon < 10^{-4}$ was achieved typically in 15-20 iterations.

It should be pointed out that the relative error of the MO wave functions is of the same order of magnitude as that of the potential. Since the total energy is variationally determined, and therefore accurate to second order in the wave functions, the degree of self-consistency we have used is sufficient to insure the accuracy required in the total energies at large R .

2. Results

In Figure 2 are displayed the interaction energies, ΔE , for the three diatoms, He-He, He-Ar and Ar-Ar, as a function of R , the internuclear separation. The interaction energies are shown for the states with the lowest energy at large R (i.e., asymptotic ground states). The interactions on this semi-logarithmic plot are seen to be quite linear, indicating the repulsion they show over the investigated ranges of R is characteristically of the Born-Mayer type, namely $A \exp(-bR)$. This behavior, of course, would break down at very small R , where the Coulomb repulsion between the nuclei becomes strongly dominant. The beginning stages of this other behavior is seen in the He-He case at $R \approx 0.7 a_0$. On the other hand, as R

Figure 2. Interaction energies, ΔE , for the pairs He-He, He-Ar and Ar-Ar in their separated atom ground states. Calculated points are encircled. a.u. of distance refers to the Bohr radius, a_0 .



increases for a given interaction and approaches the van der Waals radius, the actual interaction energy would pass through zero, and its logarithm would asymptotically approach ($-\infty$) as R nears the point of zero interaction. This pronounced deflection of the logarithm of ΔE away from the Born-Mayer straight-line behavior is not exhibited by the calculated interaction energies in Figure 2, indicating that these "muffin-tin" interaction energies show no tendency to describe the van der Waals attractive well. It should be pointed out, though, that efforts made to correct for the "muffin-tin" effects in the case of Ne-Ne have shown a well defined attractive region (Da73, Da74a, Da74b). The procedure for calculating these corrections is, however, non-trivial, and would be impractical for the present purposes.

Therefore, Born-Mayer A and b parameters for the interactions of Figure 2 were determined by means of a least-squares fit to the calculated points over the regions of straight-line behavior. The parameter b measures the slope of an interaction as shown in Figure 2, and reflects the "hardness" of the repulsion described. The parameter, A , serves as a measure of the overall strength of repulsion, being the value of $\ln(\Delta E)$ at $R=0$, although it is somewhat unrealistic, since $R=0$ is an unphysical separation at which to compare the "strength" of the repulsion of a Born-Mayer type.

So, the A parameters of the interactions of Figure 2 are simply listed in Table I, and it is pointed out that over the region of Born-Mayer behavior, they lead to interaction energies for the three diatoms which overestimate the repulsion, but obey the combination rules for such interactions in that the He-Ar Born-Mayer line falls between those of He-He and Ar-Ar. Listed in Table I by way of comparison are the b parameters of the interactions of Figure 2 along with those determined from other theoretical calculations and experiment, as indicated. The ranges over which the listed parameters apply are shown in parentheses. In general, the b parameters of the present work reflect "softer" repulsions than do the other tabulated b parameters. However, the ranges of R values of the present work extend to larger R, and it is possible that "muffin-tin" effects lead to a proportionally larger over-estimation of the repulsion at large R, i.e., to smaller b parameters.

The case of He-He is now considered in more detail. In particular, the behavior of the $MSX\alpha$ eigenenergies is looked at, providing a good example for diatomic interactions. As is well known, at large internuclear separation, the lowest state of the He-He diatom is the $1\Sigma_g^+$ state specified by doubly occupied $1\sigma_g$ and $1\sigma_u$ molecular orbitals. These two MO's are, at large R, essentially the gerade

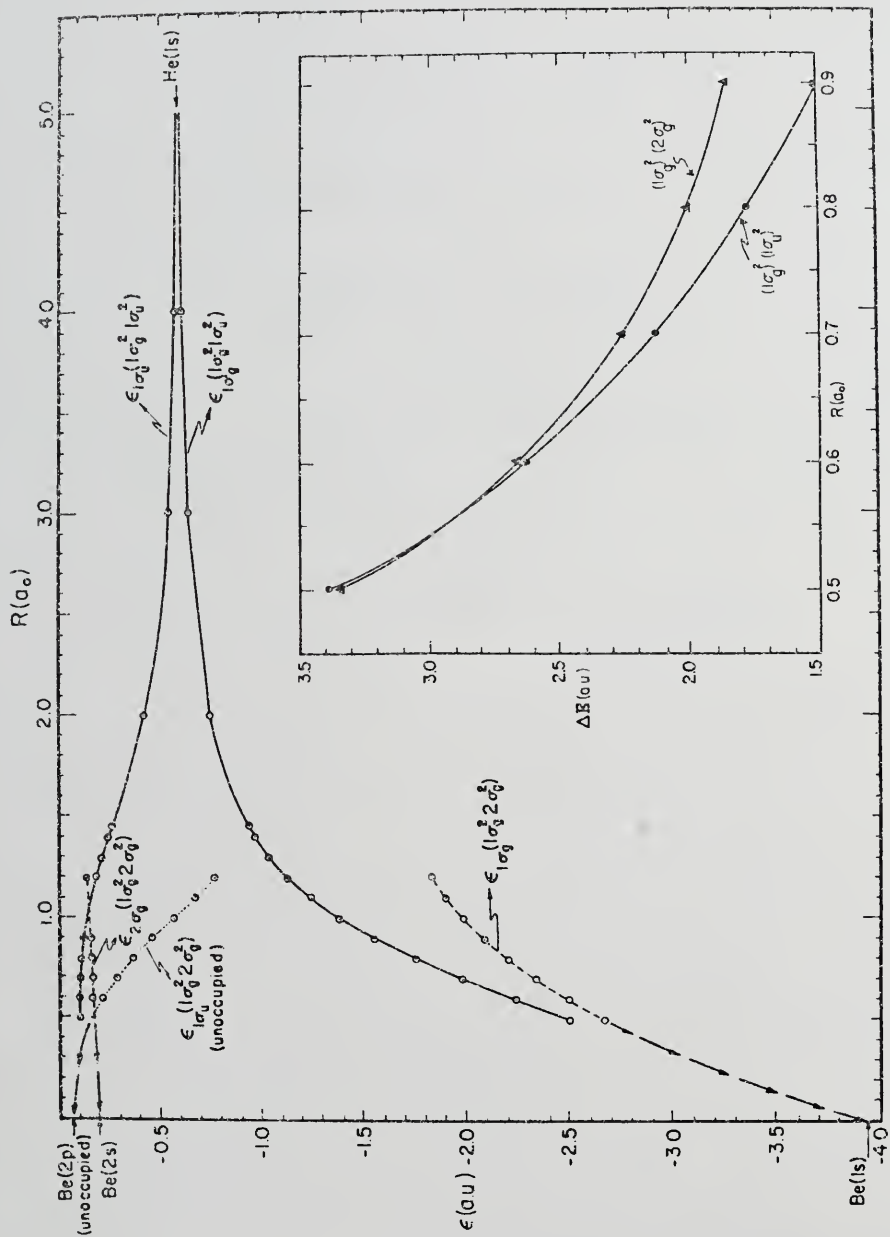
Table I: Parameters of the Born-Mayer Repulsive Interaction, $A \exp(-bR)$

PRESENT		THEORETICAL (Hartree-Fock)		THEORETICAL (Statistical)		EXPERIMENTAL	
A(a.u.)	$b(a_0^{-1})$	$b(a_0^{-1})$	$b(a_0^{-1})$	$b(a_0^{-1})$	$b(a_0^{-1})$	$b(a_0^{-1})$	$b(a_0^{-1})$
He-He	7.00 (0.7 - 5.0)	1.7065 (1.5 - 3.0)	2.1565 ^a (1.5 - 3.0)	2.7085 ^c (1.0 - 4.0)	2.2754 ^d (0.66-2.84)		
He-Ar	83.16 (2.0 - 5.0)	1.8400 (2.0 - 5.5)	1.884 ^b (2.0 - 5.5)	2.2041 ^c (1.0 - 4.5)	2.0638 ^e (2.08 - 4.0)		
Ar-Ar	216.49 (2.5 - 7.0)	1.5138 (3.0 - 5.0)	1.6726 ^a (3.0 - 5.0)	1.8651 ^c (1.0 - 5.0)	1.884 ^d (1.51 - 4.16)		

(a) Gi67; (b) Ma67b; (c) Go72; (d) Le79; (e) Co69.

and ungerade combinations of the He $1s$ atomic orbitals. In Figure 3 is shown the plot of the eigenvalues of these two orbitals as a function of R over the range $0.5 a_0$ to $5.0 a_0$. In keeping with the idea of a correlation diagram, arrows indicate the HFS atomic orbital eigenenergies; the $1s$ orbital of He in its ground $1s^2$ configuration, in the separated atom (SA) limit, and the $1s$, $2s$ and $2p$ orbitals of Be in its ground $1s^2 2s^2$ configuration in the united atom (UA) limit. It is seen that $\epsilon_{1\sigma_g}$ and $\epsilon_{1\sigma_u}$ are nearly degenerate with ϵ_{1s} of He at large R , as expected, and separate as R decreases. Now, in the UA limit, the $1\sigma_u$ orbital correlates with the Be $2p_0$ atomic orbital. Thus the $^1\Sigma_g^+$ ($1\sigma_g^2 1\sigma_u^2$) state approaches the excited Be $1s^2 2p_0^2$ atomic state in the UA limit. On the other hand the $2\sigma_g$ orbital correlates with the UA Be $1s$ atomic orbital. It is therefore the $^1\Sigma_g^+$ ($1\sigma_g^2 2\sigma_g^2$) state which in the UA limit correlates with the $1s^2 2s^2$ Be ground state. It is of interest to determine at what internuclear separation the $^1\Sigma_g^+$ state specified by $1\sigma_g^2 2\sigma_g^2$ becomes lower in energy than that specified by $1\sigma_g^2 1\sigma_u^2$. As discussed earlier in this chapter, one may proceed in two ways: (1) direct observation of the interaction energies, ΔE , of the two states as functions of R to see where they cross; or (2) observation of the eigenenergies of, for instance, the $1\sigma_g^2 2\sigma_g^2$ state to see where $\epsilon_{1\sigma_g}$ and $\epsilon_{2\sigma_g}$ become the ones of lowest

Figure 3. Orbital eigenenergies for the $1\sigma^2_{g1\sigma_u}$ and $1\sigma^2_{g2\sigma_g}$ states of He-He. Calculated points are encircled except where they are too close together, such as at 0.5 a₀ and 5.0 a₀. The insert shows interaction energies for the same two states.



value. Proceeding from $1.2 a_0$ to smaller R , the eigenenergies for the $1\sigma_g^2 2\sigma_g^2$ state have been plotted along with those of the $1\sigma_g^2 1\sigma_u^2$ state. For the $1\sigma_g^2 2\sigma_g^2$ state, $\epsilon_{1\sigma_u}$ lies lower, to begin with, than $\epsilon_{2\sigma_g}$, and Fermi statistics indicates that $1\sigma_g^2 2\sigma_g^2$ is not the state of lowest energy. However, $\epsilon_{1\sigma_u}$ is rising sharply as R decreases, and is seen to cross above $\epsilon_{2\sigma_g}$ between $0.5 a_0$ and $0.6 a_0$. Inward from this crossing the $1\sigma_g$ and $2\sigma_g$ orbitals have the lowest eigenenergies and hence the $1\sigma_g^2 2\sigma_g^2$ state has the lowest energy. For comparison, in the insert of Figure 3, a plot with linear scales is shown of ΔE versus R for these two states, which corroborates this behavior.

It should be noted that the interaction energies cross in a very gradual manner whereas the eigenenergies cross more sharply. Thus the eigenenergy behavior indicates more clearly the position of the crossing, which is found to be $0.53 a_0$. These results compare well with SCF results reported on He-He (Ma67c), where it was found that the energies of the $1\sigma_g^2 1\sigma_u^2$ and $1\sigma_g^2 2\sigma_g^2$ configurations cross near $0.6 a_0$. Also, in the accompanying 50 configuration natural-orbital iteration calculations, it was reported that the $1\sigma_g^2 1\sigma_u^2$ configuration was dominant beyond $0.7 a_0$. Though the calculations reported here go inwards only to $0.5 a_0$, the eigenenergies of the $1\sigma_g^2 2\sigma_g^2$ state are seen to be approaching the appropriate eigenenergies of ground state Be.

An investigation (Ya74) of the He-He diatom, subsequent to the one reported here (Be74a), but closely paralleling it, has been carried out in the Hartree-Fock approximation. It is interesting to compare the MSX α and Hartree-Fock results. In both approaches, the behavior of the total energies of the $1\sigma_g^2 1\sigma_u^2$ and $1\sigma_g^2 2\sigma_g^2$ configurations as R decreases from 0.6 a_0 to 0.5 a_0 shows that they cross very gradually, the energy of the $1\sigma_g^2 2\sigma_g^2$ state becoming lower than that of the $1\sigma_g^2 1\sigma_u^2$ state at 0.56 a_0 in the Hartree-Fock case, and as has been seen here, at 0.53 a_0 in the MSX α case. These values are in good agreement. However, in the Hartree-Fock approach, the determination is based solely on the total energy curves of the two states as they cross with nearly the same slope. This is because in the Hartree-Fock approach there is no immediate connection between the state of lowest energy and the eigenenergies of the MO's associated with that state. However, as has been discussed and demonstrated here, such a connection can be made in the X α approach on the basis of Equation (43), which permits the detection of crossings either by observing MO eigenenergies or total energy curves.

For Ar-Ar, at large R, the ground state is also $1\Sigma_g^+$ and is specified by the first five σ_g and σ_u MO's, each being doubly occupied, and the first two π_u and π_g

MO's, each having occupation number 4. For large R , orbitals $1\sigma_{g,u}$ to $5\sigma_{g,u}$ are formed from the appropriate combinations of Ar $1s$, $2s$, $2p_o$, $3s$ and $3p_o$ atomic orbitals, and the first and second $\pi_{g,u}$ orbitals from the appropriate combinations of Ar $2p_{\pm}$ and $3p_{\pm}$ atomic orbitals, respectively. In keeping with the Fermi statistics, the eigenenergies of these occupied orbitals are the lowest ones at large R , where we also find lying above them the eigenenergies of the unoccupied $6\sigma_g$ and $1\delta_g$ orbitals. A number of states can be specified at smaller R by the various assignments of occupation numbers to the $5\sigma_u$, $6\sigma_g$ and $1\delta_g$ orbitals.

Calculations have been made on some of these states and are displayed in Figure 4 on a semi-logarithmic plot of ΔE versus R (in Figure 4, $\sigma_u^m \sigma_g^n \delta_g^p$ refers to $5\sigma_u^m$, $6\sigma_g^n$ and $1\delta_g^p$). In the region of R shown, numerous crossings can be seen, and they are all of a very gradual type. The $\sigma_u^1 \sigma_g^1$ and δ_g^2 curves are from non-spin-polarized MSX α calculations, the corresponding spin-polarized calculations reflecting only a small splitting scarcely noticeable on such a graph as Figure 4. We can see that the SA ground state, denoted by σ_u^2 in Figure 4, no longer is of lowest energy for R less than about $3 a_o$. This can be confirmed again, by looking at the eigenenergies for this state, and in Figure 5 we display the highest of them versus R on a

Figure 4. Interaction energies, ΔE , for Ar-Ar in states where the highest orbitals have occupation numbers as specified. Calculated points are encircled. a.u. of distance refers to the Bohr radius, a_0 .

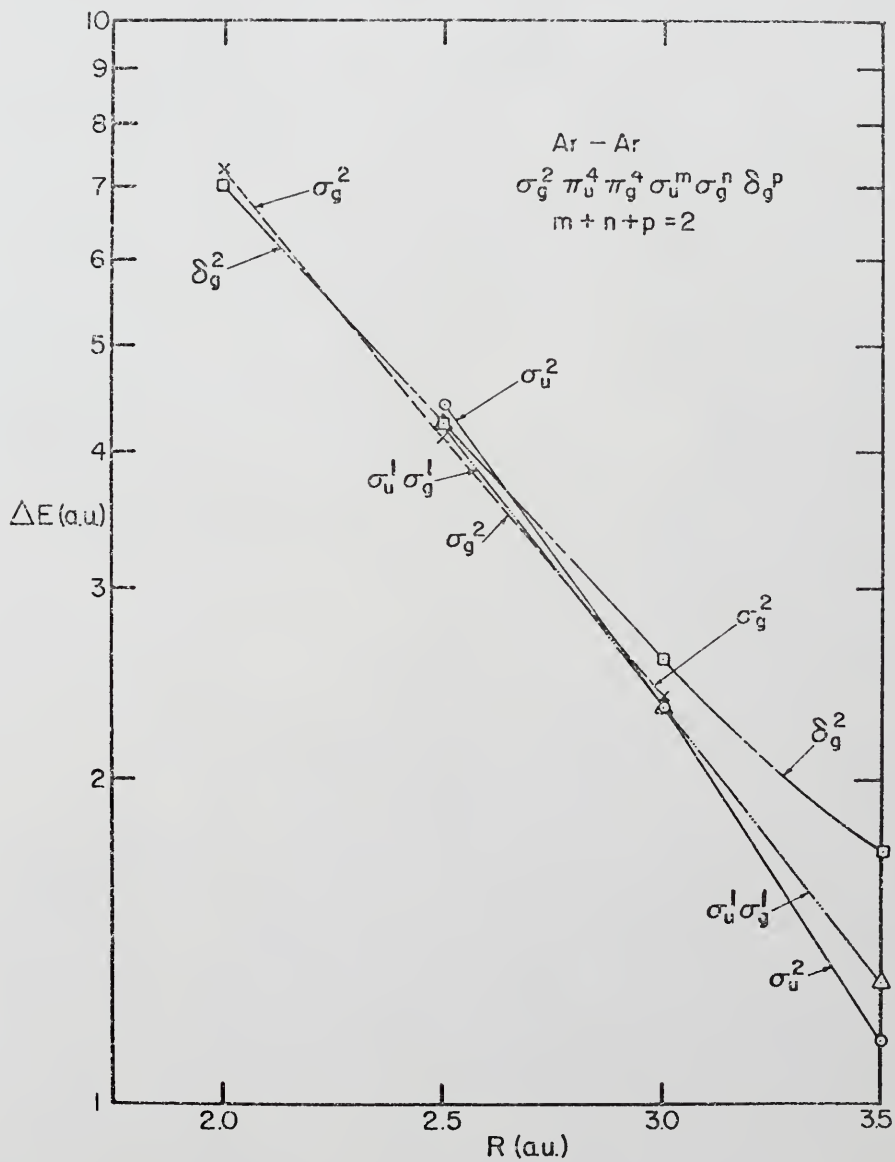
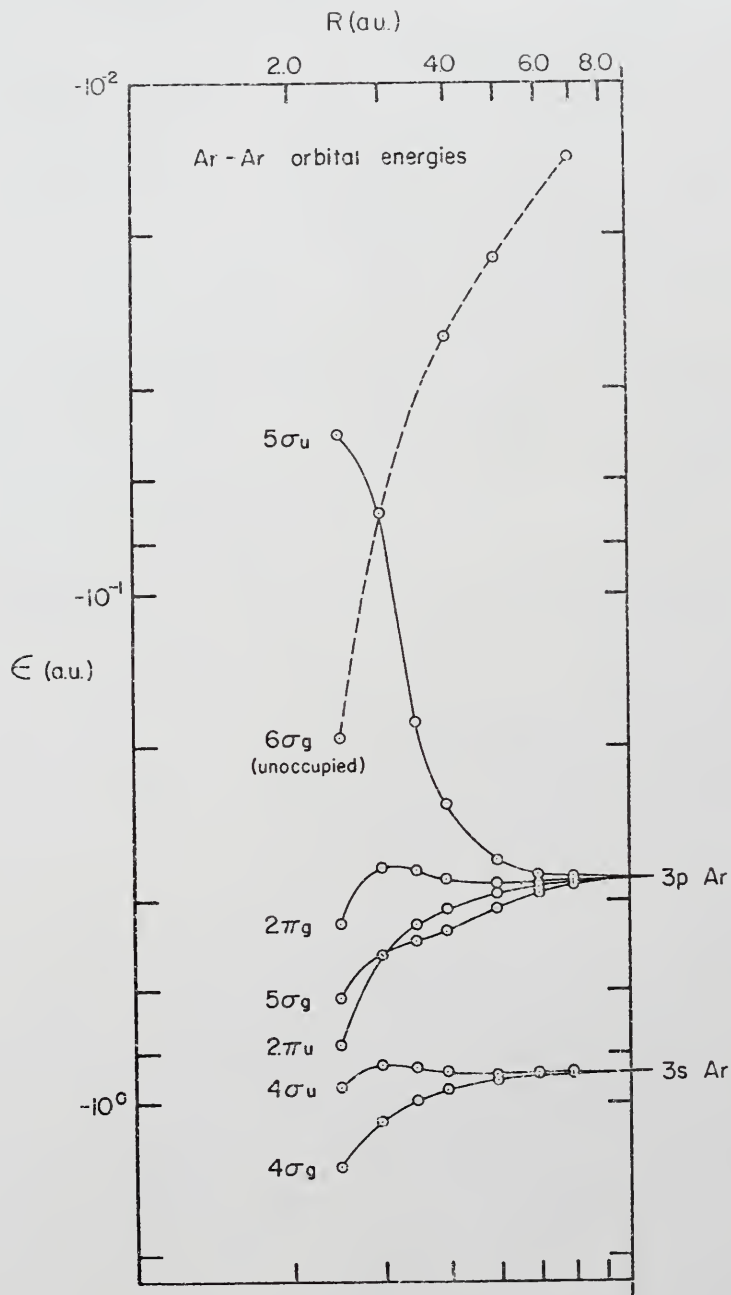


Figure 5. Orbital eigenenergies for Ar-Ar in its separated atom ground state. Calculated points are encircled. a.u. of distance refers to the Bohr radius, a_0 .



log-log plot. The appropriate SA 3s and 3p eigenenergies are also shown. The eigenenergy of the unoccupied $6\sigma_g$ MO (which, in the SA limit correlates with the unoccupied 4s atomic orbital of ground state Ar, whose orbital energy is -0.0023 a.u. and lies off the scale in the figure) is seen to be descending rapidly as R decreases, crossing the occupied $5\sigma_u$ orbital eigenenergy sharply at $3 a_0$, indicating that for R less than $3 a_0$, this state is indeed no longer of lowest energy.

3. Discussion

The results which have been presented illustrate the possibilities of the MSX_α method in the study of interactions that play a role in collision events. The interaction potentials themselves render information on the Born-Mayer type repulsion and, in conjunction with results on van der Waals attractions, enter into the calculation of relative motion of colliding atoms. Implicit in the remarks on crossings between interaction terms for various states is that the states calculated in the X_α method are diabatic in nature. Indeed this is the case since each state is independently calculated after being specified by an assignment of occupation numbers to the orbitals. So, while describing the dynamics of collision events, we can expect the largest coupling between molecu-

lar configurations to come from the electron-electron interaction. In principle, these interaction matrix elements between determinantal wave functions comprised of MSX α orbitals can be calculated, but in practice the problem at present seems quite formidable.

The usefulness of the X α orbital energies, ϵ_i , in showing where interaction potentials cross, has been shown. Hence, critical distances of approach for the occurrence of various electronic excitation phenomena can be determined. Also of interest are crossings between eigenenergies such as occurs between $\epsilon_{5\sigma_g}$ and $\epsilon_{2\pi_u}$ in Figure 5, if one or the other of the involved orbitals were partially occupied. Such crossings are of importance in electron promotion mechanisms involved in energetic atom-atom and ion-atom collisions.

Although the pairs studied here consist of closed shell atoms, it is expected that the MSX α method, because of its self-consistent treatment, can handle as well the repulsion in cases where sizable charge rearrangement takes place. Of particular interest would be the mechanisms involved in Penning and associative ionization phenomena, where atom + excited atom and ion + atom interactions are of importance. Here again, though, reliance upon additional results for describing the van der Waals region would be needed. In Chapters III and IV the considerations

prompted by the research of this chapter will be applied to an investigation of the electronic structure and collision dynamics involved in Penning ionization of $\text{Ar}(3\text{p}^6)$ by $\text{He}^*(1\text{s}2\text{s}, ^1, ^3\text{S})$.

CHAPTER III

DIATOMIC MOLECULAR ORBITAL CORRELATION DIAGRAMS FOR PENNING AND ASSOCIATIVE IONIZATION

In the previous chapter it has been pointed out that an adequate understanding of atomic and molecular collision phenomena requires information on electronic structure as a function of the changing internuclear separations. Such information is needed in order to describe inelastic processes involving electronic excitation and charge transfer as well as ionization. In this regard, the usefulness of one-electron molecular orbital (MO) approaches in treating electronic structure was emphasized. Such approaches afford a self-consistent calculational framework of minimal complexity which can treat ground as well as excited states. Chemionization is a prime example of processes where electronically excited states play a crucial role. In this chapter* the electronic structure involved in a collisional process of this type will be considered.

Well known among chemi-ionization processes are Penning and associative ionization (PI and AI) of the type

*A preliminary report of the results presented in this chapter was made at the International Symposium on Atomic, Molecular and Solid State Theory, Collision Phenomena and Computational Methods held at Sanibel Island, Florida, 18-24 January 1976.

$A^* + B \rightarrow A + B^+ + e^-$ (PI) and $A^* + B \rightarrow AB^+ + e^-$ (AI), where A^* is usually an atom in some metastable state and B is an atom or molecule (Mu66, Mu68, Mu73, Ni73, Be70a, Be70b, Ru72, Ma76). Experimental information for such collisions includes total ionization cross-sections as a function of collision energy (Ta72, Ch74, Pe75, Il75), angular distributions of heavy particles (Ha73), and energy distribution (Ho70, Ho75, Ce71) and angular distribution (Ho71, Eb74) of emitted electrons. Most theoretical effort has been directed at determining the energy dependence of total ionization cross-sections and the angular distribution of heavy particles (Na69, Mi70b, Mi71, Ol72a). The angular distribution of emitted electrons has been recently studied within a semiempirical model based on MO correlation diagrams (Mi75). One of the present concerns is to re-emphasize the usefulness of MO correlation diagrams as they apply to angular distribution of ejected electrons in PI and AI involving atomic collision partners.

In what follows, calculated as well as estimated MO correlation diagrams are presented. The calculated results are given first, where the electronic structure of $He^*(1s2s, ^1, ^3S) + Ar(3p^6, ^1S)$ has been considered within the MSX α framework as described in the previous chapter. A study has been made, in the non-spin-polarized approximation, of the $K_{Ar}L_{Ar}(\sigma1sHe)^1(\sigma3sAr)^2(\sigma3pAr)^2(\pi3pAr)^4(\sigma2sHe)^1$

configuration of the excited He-Ar diatom whose MO eigenenergies approach the atomic orbital eigenenergies of $\text{He}^*(1s2s)$ and $\text{Ar}(3p^6)$ at large internuclear separation, and also the ground $^2\Sigma$ state of the $(\text{He-Ar})^+$ molecular ion, whose MO eigenenergies approach the atomic levels of $\text{He}(1s^2)$ and $\text{Ar}^+(3p^5)$ at large internuclear separation. Some spin-polarized calculations are presented in the neighborhood of a crossing exhibited by the non-spin-polarized calculations, along with some comments on the conditions under which the non-crossing rule applies for MO eigenenergies.

Keeping in mind the calculated results, consideration is given to PI and AI processes in terms of MO correlation diagrams. Analyzing the ionization on the basis of an Auger type process, MO's can be identified, which, together with the continuum state of the emitted electron, are involved in the process. Inspecting the united-atoms limit in the center-of-mass, body-fixed frame then permits a determination of the angular momenta which contribute to the continuum state of the emitted electron.

Next a procedure for estimating MO correlation diagrams is described, which makes use of available data on atomic orbital energies, and of two basic guidelines. Application is made to the collision pairs $\text{He}^*(1s2s) + \text{Ar}(3p^6)$, $+ \text{Kr}(4p^6)$, $+ \text{Hg}(6s^2)$, and $\text{Ne}^*(2p^53s) + \text{Ar}(3p^6)$.

The resulting estimated MO correlations for these systems are then analyzed to determine the minimal set of angular momentum l values which are needed in each case to describe emitted electrons in the body-fixed frame. Finally, a discussion is given of the results of this work and their significance.

1. MO Calculations for $\text{He}^* + \text{Ar}$ and $\text{He} + \text{Ar}^+$

The representative case of PI and AI in $\text{He}^*(1s2s, {}^1, {}^3S) + \text{Ar}(3p^6, {}^1S)$ collisions will be considered. Here, calculations are needed for the excited states of the He-Ar diatom which separate appropriately to $\text{He}^*(1s2s, {}^1, {}^3S)$ and $\text{Ar}(3p^6, {}^1S)$, and for the states of $(\text{He-Ar})^+$ which separate to $\text{He}(1s^2, {}^1S)$ and $\text{Ar}^+(3p^5, {}^2P)$. Following the work reported in the previous chapter, the calculations are performed within the MSX α one-electron MO framework.

For convenience in this chapter, the set of one-electron equations satisfied by the spin orbitals, u_i , and expressed in Equation (40), are written

$$h_{\text{eff}}^\dagger(\vec{r}_1) u_i(\vec{r}_1) = \epsilon_i u_i(\vec{r}_1) \quad . \quad (45)$$

Here, $h_{\text{eff}}^\dagger(\vec{r}_1)$ is the effective one-electron Hamiltonian for electrons of spin-up, and according to Equation (40),

$$h_{\text{eff}}^{\uparrow}(\vec{r}_1) = f_1(\vec{r}_1) + \int d\vec{r}_2 \{ 2\rho(\vec{r}_2)/r_{12} \} + v_{X\alpha}^{\uparrow}(\vec{r}_1) , \quad (46)$$

where $v_{X\alpha}^{\uparrow}(\vec{r}_1)$ is given by Equations (42) and (39), and $\rho(\vec{r})$, given by Equation (38), is the charge density comprised of the contributions from electrons of spin-up and spin-down. In the non-spin-polarized (NSP) approximation,

$$\rho^{\uparrow}(\vec{r}) = \rho^{\downarrow}(\vec{r}) = \rho(\vec{r})/2 , \quad (47)$$

which means that the orbitals of spin-up and spin-down become identical, and each orbital can be considered as accommodating as many electrons of spin-up as of spin-down.

These calculations were carried out first with a NSP treatment. As discussed in the previous chapter, each self-consistent calculation begins with a potential which is the "muffin-tin" form of a superposition of atomic potentials centered at each atomic site of the molecule. Therefore, for the He-Ar excited state $\text{Ar}(3p^6)$ and NSP $\text{He}^*(1s2s)$ Hartree-Fock-Slater (HFS) (He63) potentials were used, and for the He-Ar ionic state $\text{He}(1s^2)$ and NSP $\text{Ar}(3p^5)$ HFS potentials were used. For both the excited molecule and the molecular ion, the electronic states were specified by occupying the MO's so that their eigenenergies were correctly separating at large internuclear separations to the corresponding atomic orbital eigenenergies of the above mentioned HFS atomic calculations. In other words, the

boundary conditions of the PI and AI processes at large R determined the appropriate excited and ionic states of the He-Ar molecule. Heteronuclear molecules require a choice for the radii of the spherical regions centered at each atomic site as mentioned in the previous chapter. There, for the ground state He-Ar molecule, the ratio of the He to the Ar sphere radii was taken to be $\langle r_{1s} \rangle_{\text{He}} / \langle r_{3p} \rangle_{\text{Ar}} \approx 0.92727/1.66296 \approx 0.5576$, where, e.g. $\langle r_{1s} \rangle_{\text{He}}$ denotes the average value of r for the $1s$ orbital of $\text{He}(1s^2)$. The situation for $(\text{He-Ar})^+$ is roughly the same as for He-Ar, since a calculation of $\langle r_{3p} \rangle$ for $\text{Ar}^+(3p^5)$ (NSP) shows it to be $1.549 a_0$. So, for the molecular ion the ratio of 0.5576 was used at all R . On the other hand $\text{He}^*(1s2s) + \text{Ar}(3p^6)$ is quite another case, since the $2s$ orbital of $\text{He}^*(1s2s)$ is very diffuse. NSP calculations show $\langle r_{2s} \rangle$ of $\text{He}^*(1s2s)$ to be about $4.546 a_0$. Because of this diffuseness, it was decided to choose the ratio of the He to the Ar sphere radii by finding which of its values minimized the total energy of the specified excited state of He-Ar at a fairly large R , namely $R = 9.0 a_0$. In this way, a ratio of 1.4 was found, which was then used at all R for the excited state of He-Ar. The values of the factor α in the various "muffin-tin" regions of the molecule, for both the excited as well as ionic states, were those used previously in the ground state He-Ar calculations, and the specific computa-

tional details also remain as reported in the previous chapter.

The results of the NSP MSX α calculations are displayed in Figures 6 and 7, respectively, for the excited state of the He-Ar diatom and the ground state of the He-Ar molecular ion which are appropriate to PI and AI. Shown on log-log plots are the MO eigenenergies versus R for $2.3 a_0 \leq R \leq 10.0 a_0$ in the case of the excited molecule and $2.0 a_0 \leq R \leq 6.0 a_0$ in the case of the molecular ion. The MO eigenenergies are labeled according to their symmetry and occupation number. In each case, the NSP HFS atomic orbital eigenenergies for the separated atoms are shown at the right of the plot, and the dashed lines indicate how each MO eigenenergy is approaching properly its respective separated-atoms (SA) limit. In the united-atoms (UA) limit the excited He-Ar molecule is expected to approach $\text{Ca}^*(3p^5 4s^2 3d)$, and the ground state molecular ion to approach $\text{Ca}^+(3p^6 4s)$. The atomic orbital eigenenergies from NSP HFS calculations on these united atoms are appropriately shown at the left of each plot, and, while the MO eigenenergies may exhibit much structure between the region of $2 a_0$ and the UA limit, the dashed lines at the left of each plot show that these UA limits are not unreasonable. In both plots, the label for the σ MO arising at large R from $3p_{\text{Ar}}$ appears above the π MO label. In fact,

Figure 6. Molecular orbital correlation diagram from non-spin-polarized MSX α calculations of the He-Ar diatom in the excited Σ configuration which separates at large R to He*(1s2s) + Ar(3p⁶). Calculated points are encircled.

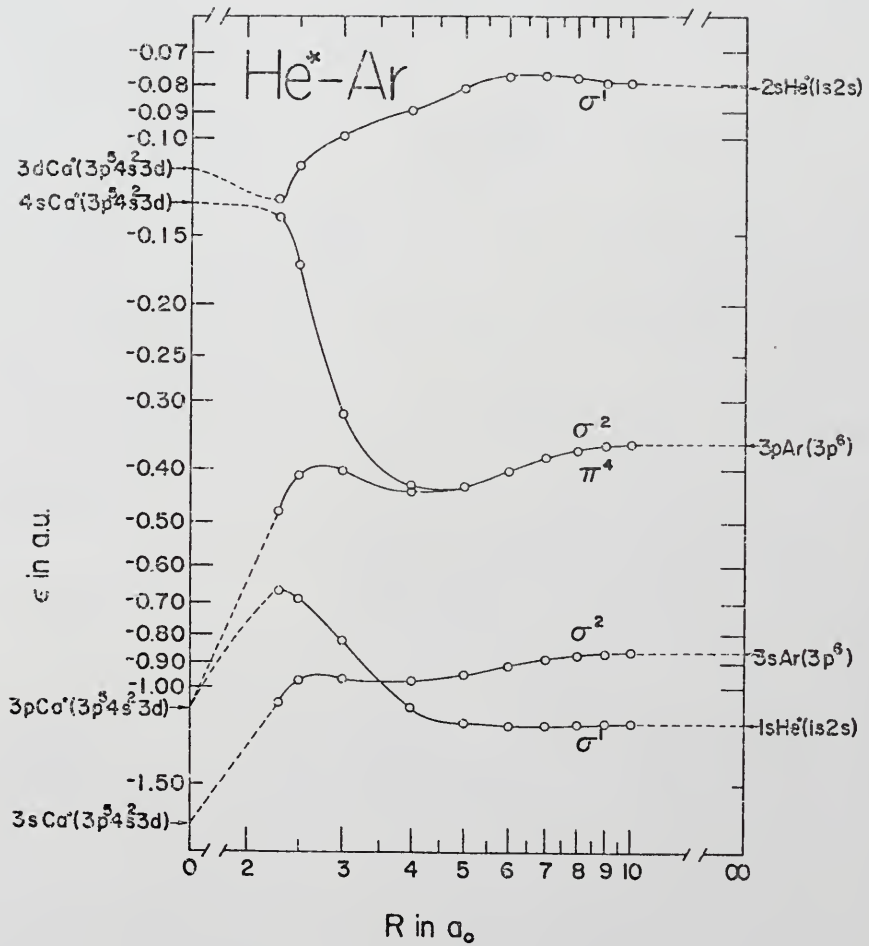
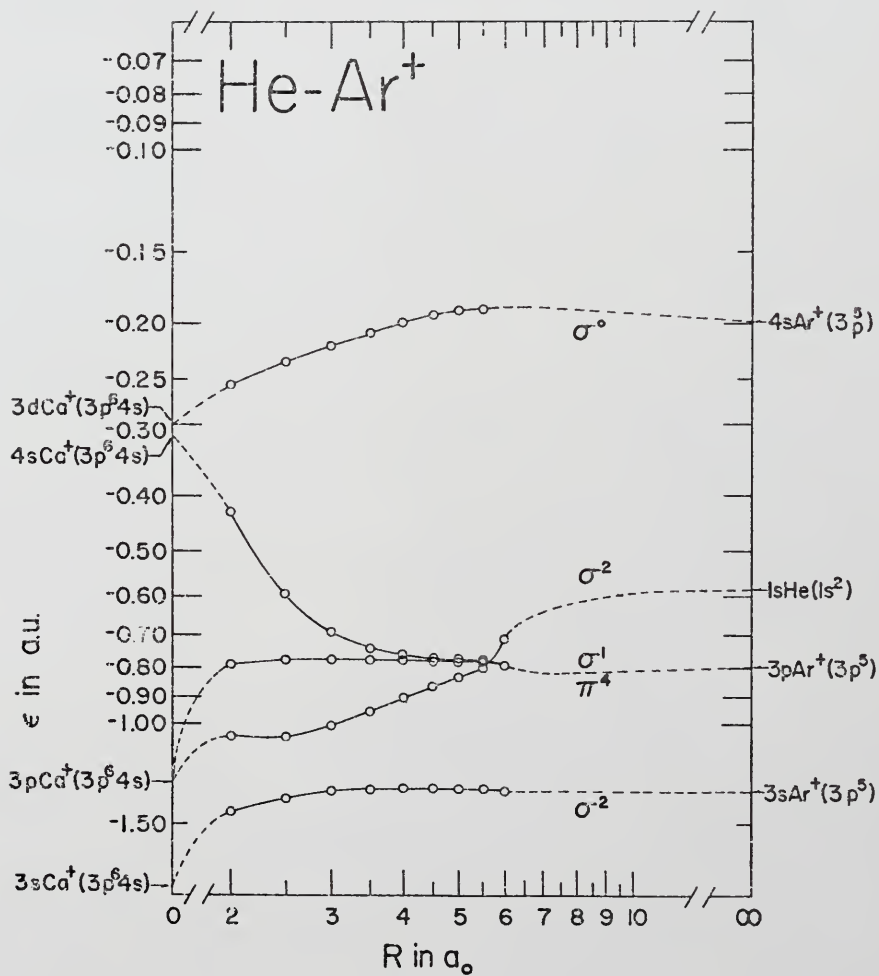


Figure 7. Molecular orbital correlation diagram from non-spin-polarized MSX α calculations of the (He-Ar)⁺ molecular ion in the ground Σ state which separates at large R to He(1s²) + Ar⁺(3p⁵). Calculated points are encircled.



this ordering for those levels is valid only for $R \lesssim 5 a_0$. For $R \gtrsim 6 a_0$, the π level lies above the σ level, but they are too close together at large R to be distinguishable on these plots.

In Figure 6 a crossing is shown near $3.5 a_0$ occurring between the doubly and singly occupied NSP σ orbitals arising respectively at large R from $3sAr(3p^6)$ and NSP $1sHe^*(1s2s)$. This crossing would appear to violate the non-crossing rule for the MO eigenenergies, and warrants a detailed analysis. The orbitals of a given symmetry are ordered according to their eigenenergies, obtained self-consistently from Equation (45). This equation is an eigenvalue equation involving an effective Hamiltonian determined at each R according to Equation (46). To establish the non-crossing rule for the eigenenergies of Equation (45), one expresses the effective Hamiltonian at a supposed crossing, R_c , in terms of its expansion about $R = R_c + \delta R$ located a small distance, δR , from R_c :

$$h_{\text{eff}}^{\uparrow}(R_c) = h_{\text{eff}}^{\uparrow}(R) - (dh_{\text{eff}}^{\uparrow}/dR)_{R_c} \delta R \quad . \quad (48)$$

The non-crossing rule follows by noticing that $(dh_{\text{eff}}^{\uparrow}/dR)_{R_c} \delta R$ is a perturbation which lifts any degeneracy in the eigenvalue spectrum at R_c . However, if $h_{\text{eff}}^{\uparrow}(R)$ is made to be discontinuous by choice, the conditions of the non-crossing rule no longer apply.

Referring to Equation (46), the R dependence of the effective Hamiltonian appears explicitly in $f_1(\vec{r}_1)$ (see Equation (41)) and implicitly in the charge density, ρ .

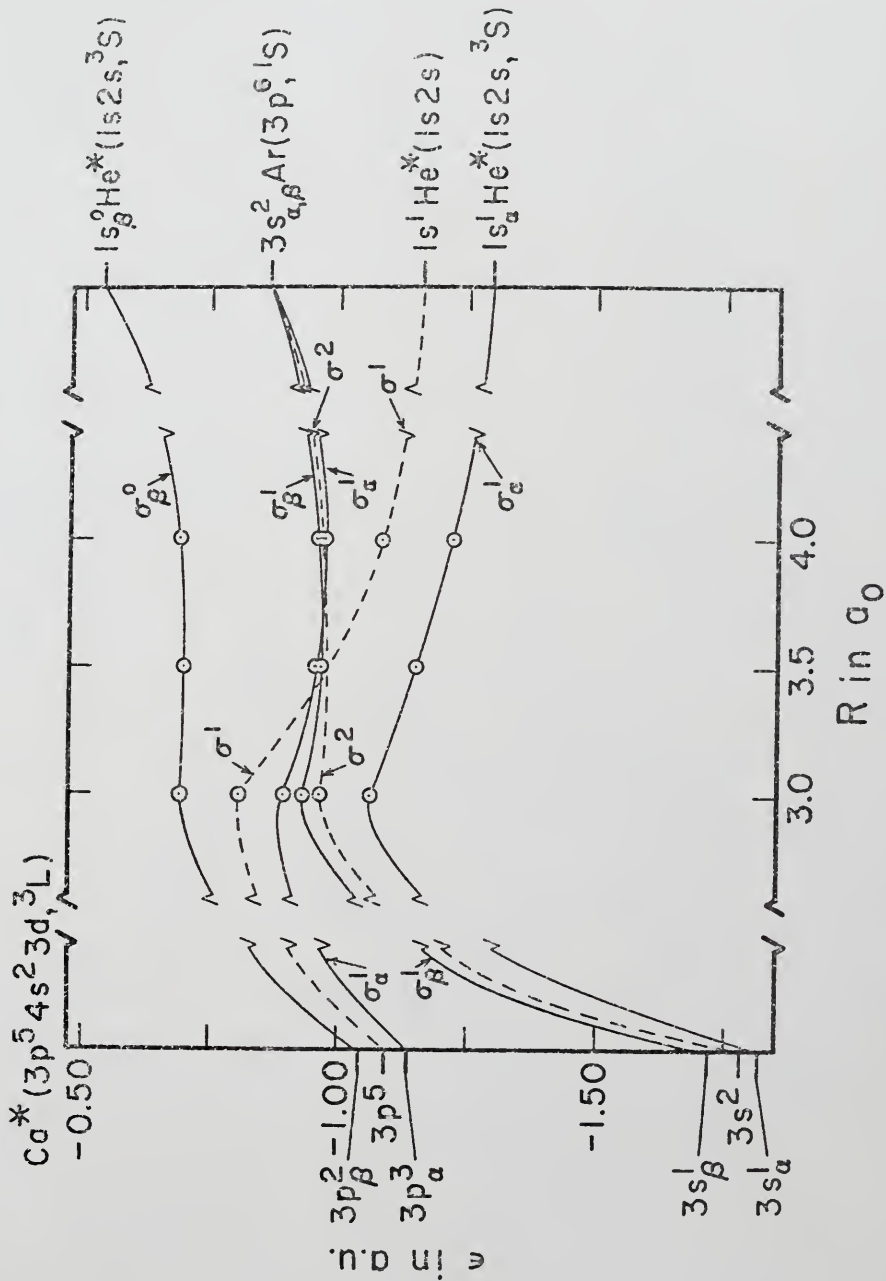
Showing the full R dependence, the effective Hamiltonian may be written as $h_{\text{eff}}^{\dagger}\{\vec{r}_1; R, \rho(\vec{r}_1, R)\}$, and

$$dh_{\text{eff}}^{\dagger}/dR = \partial h_{\text{eff}}^{\dagger}/\partial R|_{\rho} + (\delta h_{\text{eff}}^{\dagger}/\delta \rho)(d\rho/dR) \quad . \quad (49)$$

The term, $d\rho/dR$, in Equation (49) can be seen, from Equation (38), to involve derivatives of the orbitals and occupation numbers with respect to R . As long as the n_i and u_i are continuous in their R dependence, $dh_{\text{eff}}^{\dagger}/dR$ will be well behaved, and the non-crossing rule will hold. However, if the occupation numbers are changed discontinuously in some region of R , then the non-crossing rule will no longer be valid in that region. These considerations apply as well to the NSP effective Hamiltonian and in fact, in the case at hand, as shown in Figure 6, a discontinuous change in occupation numbers does occur. To the right of the crossing, the σ orbitals, in order of increasing eigenenergy, have occupation numbers 1, 2, 2 and 1. To the left of the crossing, they are 2, 1, 2 and 1. A further investigation of the region of the crossing was made by doing spin-polarized calculations at $R = 3.0 a_0$, $3.5 a_0$ and $4.0 a_0$ in the case of the $^3\Sigma$ excited state which separates at large R to $\text{Ar}(3p^6, ^1S)$ and $\text{He}^*(1s2s, ^3S)$. In Figure 8 attention is restricted to the levels of the NSP σ^2 and σ^1 MO's which cross in Figure 6, and they are contrasted with their spin-split counterparts calculated in

Figure 8.

Spin-polarized (solid lines) molecular orbital eigenenergies calculated for the excited 3γ configuration of the He-Ar diatom which separates at large R to $\text{He}^*(1s2s, 3S) + \text{Ar}(3p^6, 1S)$, and their non-spin-polarized counterparts (dashed lines) from Figure 6. The eigenenergies are those arising at large R from the $1s\text{He}^*$ and $3s\text{Ar}$ atomic orbitals, and are shown in the neighborhood of the crossing near 3.5 a.u. in Figure 6. Those associated with spin-polarized orbitals are labeled according to their spin (α or β). Calculated points are encircled.



the region $3.0 a_0 < R < 4.0 a_0$ as well as at the UA and SA limits.

Important to notice is that for $R > 3.5 a_0$ the NSP σ^1 orbital of He^* is split considerably into its occupied component of spin-up σ_α^1 and its unoccupied component of spin-down σ_β^0 , on out to the SA limit, where the splitting is between the unoccupied $1s_\beta$ and the occupied $1s_\alpha$ of $\text{He}^*(1s2s, {}^3S)$. The σ^2 orbital from Ar is split only slightly into each of its occupied spin components. Crossings between two orbital eigenenergies of different spin components are permitted since each involves a different effective Hamiltonian (see Equation (46)). Between $3.5 a_0$ and $4.0 a_0$ we find such a crossing for the two spin components that split from the NSP σ^2 orbital of Ar, and in fact, as R decreases, the σ_β^1 level from $3s\text{Ar}(3p^6, {}^1S)$ is decreasing in energy to pair up with the occupied σ_α^1 level from $1s_\alpha\text{He}^*(1s2s, {}^3S)$, whereas its spin-up partner from $3s_\alpha\text{Ar}(3p^6, {}^1S)$ is rising to pair up with the (empty) σ_β^0 level from $1s_\beta\text{He}^*(1s2s, {}^3S)$. In the UA limit, this empty σ_β^0 level will correlate with the partially occupied $3p_\beta$ atomic orbital of $\text{Ca}^*(3p^5 4s^2 3d, {}^3L)$, where L here denotes one of the possible orbital angular momenta of the excited Ca atom.

Such a spin-polarized analysis as this confirmed the choice of occupation numbers of the NSP calculations for which the vacancy associated with the NSP σ^1 orbital is

correlating in the UA limit with the partially occupied 3p atomic orbital of $\text{Ca}^*(3p^5 4s^2 3d)$. This feature will prove important for the considerations later on regarding the angular momentum contributions to the continuum state of the electron emitted during PI and AI. The crossing shown in Figure 7, between the NSP singly and doubly occupied σ orbitals of the molecular ion near $5.5 a_0$, is another example of a discontinuous change in occupation numbers, which in this case is required to reach the appropriate SA limit.

2. Analysis of PI and AI Processes Based on MO Correlation Diagrams

Consideration is given now to how an MO correlation diagram study, such as has just been described, can help in understanding what takes place in PI and AI processes. Collisional ionization occurs for R greater than the distance of closest approach, which in the case of $\text{He}^* + \text{Ar}$ is around $7 a_0$ at thermal collision energies. Referring to the calculated MO diagram in Figure 6, one can see that in this range of R there is a vacancy associated with the σ^1 MO arising from $1s\text{He}^*$ at large R , above which are some fully occupied MO's as well as the singly occupied σ^1 MO arising from $2s\text{He}^*$ at large R . This situation suggests that the ionization may proceed by an Auger type process. Namely, two electrons in higher lying orbitals participate

in ionization as one of them is promoted to a continuum state while the other drops to fill a vacancy, in this case associated with the σ^1 MO arising from SA 1sHe*. The process may be characterized as one in which initially the two electrons are in MO's u_1 and u_2 , while finally (after ionization) they are in MO's u_1' and u_2' , where u_1' designates the continuum state of the ionized electron, having momentum k and angular momentum components l_1' .

If the wave function $\phi_a(N)$ is associated with the system of N electrons before ionization, and $\phi_b(k, N-1)$ is associated with the system of $(N-1)$ electrons plus the emitted electron in its continuum state after ionization, then, in the body-fixed (BF) frame, the transition probability for ionization involving these two wave functions is expressed in terms of the interaction matrix element, $V_{ba}(R, k)_{BF}$, where

$$V_{ba}(R, k)_{BF} = \langle \phi_b(k, N-1) | H_{el} - E | \phi_a(N) \rangle_{BF} \quad (50)$$

Here H_{el} is the electronic Hamiltonian for the N electrons, E is the total energy, and the brackets indicate integration over electronic variables. Within a single determinant description, ϕ_b will differ from ϕ_a in that the one electron orbitals u_1 and u_2 of ϕ_a are replaced by u_1' and u_2' to obtain ϕ_b . As a consequence Equation (50) reduces to a sum of direct and exchange contributions which can be written respectively, as

$$V_D(R,k) = \langle u_1' u_2' | v | u_1 u_2 \rangle_{BF}$$

$$V_E(R,k) = \langle u_1' u_2' | v | u_2 u_1 \rangle_{BF} , \quad (51)$$

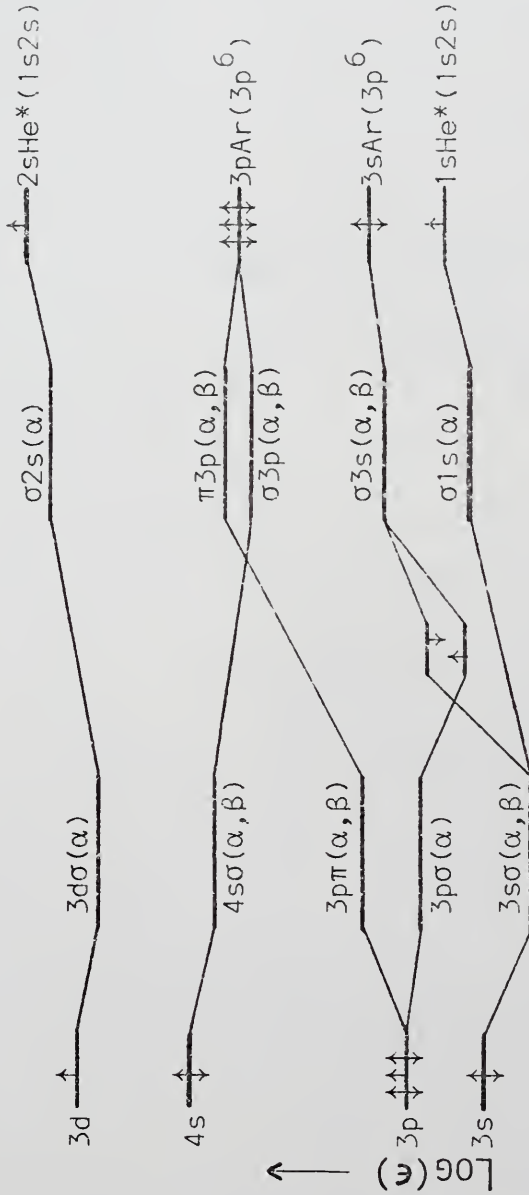
where $v = 1/r_{12}$, the electron-electron Coulomb interaction in atomic units.

In Figure 9a is shown a schematic MO correlation diagram for the $\text{He}^*(1s2s) + \text{Ar}(3p^6)$ case. The construction of such estimated MO correlation diagrams will be discussed in the next section. The MO energies at large R represent levels at the time of ionization. For instance, referring to Figure 9a, two electrons, one initially in $\sigma 2s$ from He^* and the other in $\pi 3p$ from Ar could participate in an Auger process whereby one is promoted to a continuum state while the other fills the $1s$ vacancy from He^* . That is, $u_1 = \sigma 2s$, $u_2 = \pi 3p$, the continuum state $u_1' = (k, \ell_1', m_1')$ and $u_2' = \sigma 1s$.

MO correlation diagrams, such as shown in Figure 9a, allow one to predict the minimal number of angular momentum contributions, ℓ_1' , which is necessary to describe the continuum state of the emitted electron in the BF frame. One proceeds by following the MO's involved in ionization towards their UA limit. With the exception of the continuum state, u_1' , the MO's correlate in the UA limit to atomic orbitals of well defined angular momentum. That is, one can write

Figure 9a. Estimated molecular orbital correlation diagram for $\text{He}^*(1s2s) + \text{Ar}(3p6)$.

$\text{He}^* - \text{Ar} \quad (\alpha)$

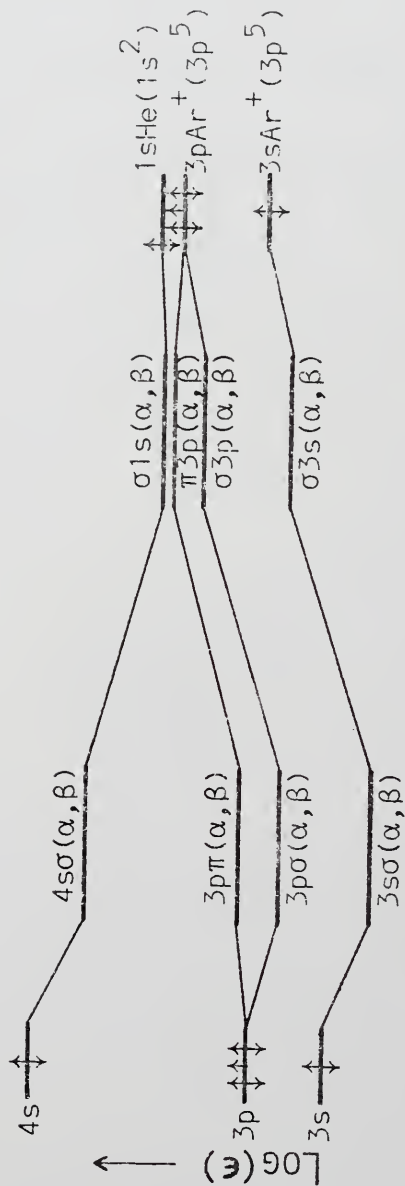


$R \longrightarrow$

$\text{Ca}^*(3p^5 4s^2 3d)$

Figure 9b. Estimated molecular orbital correlation diagram for $\text{He}(1s^2) + \text{Ar}^+(3p^5)$.

He - Ar⁺ (b)



[Ca⁺]* (3p⁵4s²) R →

$$\begin{aligned}
 u_1 & \xrightarrow{UA} \chi_1(\ell_1, m_1), \\
 u_2 & \xrightarrow{UA} \chi_2(\ell_2, m_2), \\
 u_1' & \xrightarrow{UA} \chi_1'(k, \ell_1', m_1') \text{ (continuum)}, \\
 u_2' & \xrightarrow{UA} \chi_2'(\ell_2', m_2'),
 \end{aligned} \tag{52}$$

where the χ 's refer to the UA (atomic) orbitals. Looking also at the direct and exchange matrix elements in the UA limit, Equation (51) becomes

$$\begin{aligned}
 V_D(R, k) & \xrightarrow{UA} V_D^{UA}(k) = \langle \chi_1' \chi_2' | v | \chi_1 \chi_2 \rangle_{BF} \\
 V_E(R, k) & \xrightarrow{UA} V_E^{UA}(k) = \langle \chi_1' \chi_2' | v | \chi_2 \chi_1 \rangle_{BF} .
 \end{aligned} \tag{53}$$

Next, using the notation of previous work by Micha (Mi70a), the electron-electron Coulomb interaction is expressed as an expansion in terms of its multi-pole components,

$$1/r_{12} = (1/r_>) \sum_{L=0}^{\infty} (r_</r_>)^L P_L(\cos \theta_{12}) , \tag{54}$$

and Equation (53) is written as follows:

$$\begin{aligned}
 V_D^{UA}(k) & = \delta(s_1', s_1) \delta(s_2', s_2) \sum_{L=0}^{\infty} F_L(1'2'12) A_L(1'2'12) \\
 V_E^{UA}(k) & = \delta(s_1', s_2) \delta(s_2', s_1) \sum_{L=0}^{\infty} F_L(1'2'21) A_L(1'2'21) .
 \end{aligned} \tag{55}$$

The factors F_L and A_L are proportional to products of 3-j coefficients:

$$F_L(1'2'12) = \frac{\sqrt{(2\ell_1'+1)(2\ell_2'+1)(2\ell_1+1)(2\ell_2+1)}}{2L+1} \begin{pmatrix} \ell_1' & L & \ell_1 \\ 0 & 0 & 0 \end{pmatrix}_x$$

$$\begin{pmatrix} \ell_2' & L & \ell_2 \\ 0 & 0 & 0 \end{pmatrix} R_L(1'2'12) ,$$

$$A_L(1'2'12) = (-1)^{m_1' + m_2' + M} (2L+1) \begin{pmatrix} \ell_1' & L & \ell_1 \\ -m_1' & -M & m_1 \end{pmatrix} \begin{pmatrix} \ell_2' & L & \ell_2 \\ -m_2' & M & m_2 \end{pmatrix} . \quad (56)$$

The $R_L(1'2'12)$ are Coulomb integrals involving the radial parts of the orbitals in the UA limit, and depend on their principal as well as angular momentum quantum numbers.

The presence of the 3-j coefficients in the F_L and A_L factors of Equation (56) reflects the coupling of the angular momenta of the electrons due to the 2^L multipole component of the electron-electron Coulomb interaction and allows one to specify the ranges of values of ℓ_1' and m_1' for which contributions will appear in the direct and exchange matrix elements of Equation (55). This is accomplished by employing the selection rules for the 3-j coefficients (see, for example, Me66). In the UA limit, (ℓ_1, m_1) , (ℓ_2, m_2) and (ℓ_2', m_2') are known. Therefore, referring to Equation (56), one of the 3-j factors in F_L specifies the allowed range of L , and similarly, one of the 3-j factors in A_L further specifies the range of M . Once the ranges of L and M have been determined, the remaining 3-j coefficient factors, one in F_L and one in A_L , specify the ranges of ℓ_1' and m_1' for the continuum state of the emitted electron.

Thus, for the direct matrix element of Equation (55),
L and M are restricted as follows:

$$\begin{aligned} |\ell_2' - \ell_2| &\leq L \leq \ell_2' + \ell_2 \\ (\ell_2' + \ell_2 + L) &\text{ even} \\ -m_2' + M &= -m_2 \end{aligned} \quad (57)$$

For each L and M possible from Equation (57), the remaining two factors in F_L and A_L restrict ℓ_1' and m_1' in similar fashion:

$$\begin{aligned} |\ell_1' - L| &\leq \ell_1' \leq \ell_1 + L \\ (\ell_1' + L + \ell_1) &\text{ even} \\ m_1' + M &= m_1 \end{aligned} \quad (58)$$

Interchanging the indices 1 and 2 among the primed symbols in Equations (57) and (58) provides corresponding expressions for the exchange matrix element of Equation (55).

Thus far the discussion has only been in terms of the interaction matrix element of Equation (50) between two determinantal wave functions, ϕ_a and ϕ_b , distinguished from one another, respectively, by the MO's u_1 and u_2 before ionization and u_1' and u_2' after ionization.

Consideration is now given to the manifold of determinantal states ϕ_a which is needed to represent the electronic state ϕ_i before ionization. Each of those states ϕ_a has an angular momentum component along the molecular axis, Λ_a , equal to the absolute value of the sum of axial angular

momentum components of the MO's from which the determinantal wave function is constructed. To the extent that one may neglect rotational Born-Oppenheimer couplings, only determinants ϕ_a having $\Lambda_a = \Lambda_i$ are needed in representing the state of the electrons prior to ionization, where Λ_i denotes the axial component of electronic angular momentum in the SA limit of the incident channel. However, Born-Oppenheimer couplings cannot be neglected in the UA limit because of their R^{-2} dependence (Sm69, Si76). Hence, in order to properly carry out the UA analysis just described one must include contributions from states ϕ_a for which $\Lambda_a - \Lambda_i = 0, \pm 1$.

For example, according to the MO correlation diagram of Figure 9a, one constructs the leading determinantal wave function prior to ionization from the MO's shown at the right which correlate to the occupied SA atomic orbitals, and observes that $\Lambda_i = 0$. As was mentioned earlier, there is the possible case of an Auger type process in which the participating orbitals u_1 and u_2 are identified with $\sigma 2sHe^*$ and $\pi 3pAr$, respectively. Not shown in Figure 9a are levels of MO's associated with unoccupied SA atomic orbitals. Among these MO's there may be one whose axial component of angular momentum differs by ± 1 from that of an occupied MO with which it shares the same UA atomic orbital limit. An example of such a case is the $\pi 2p$ MO

arising from the unoccupied SA 2p orbital of $\text{He}^*(1s2s)$, together with the $\sigma 2s$ MO of Figure 9a, both of which correlate in the UA limit to the singly occupied 3d atomic orbital of $\text{Ca}^*(3p^5 4s^2 3d)$. Replacing the $\sigma 2s$ MO of the previously described Σ determinant by this $\pi 2p$ MO would result in a Π determinant which is significant for the present UA analysis due to Born-Oppenheimer couplings. In the Σ case, u_1 of the Auger type process would be identified with $\sigma 2s$, in the Π case with $\pi 2p$. According to Equation (52), the UA limit results in $\ell_1 = 2, m_1 = 0$ for the Σ case and $\ell_1 = 2, m_1 = \pm 1$ for the Π case. This means that in applying Equations (57) and (58) for these two cases, the restrictions on the ℓ -values are the same for both, while the m -value restrictions involve $m_1 = 0$ for Σ and $m_1 = \pm 1$ for Π determinants.

In general, then, the UA analysis of the angular momentum contributions to the emitted electron requires that the initial electronic state prior to ionization be written as a linear combination of such determinants;

$$\phi_i = \sum_a \phi_a C_a \quad . \quad (59)$$

Similar considerations hold after ionization, where a manifold of determinants ϕ_b results, each differing from the other by the particular continuum state u'_1 associated with it. The final electronic state then is written,

$$\phi_f = \sum_b \phi_b C_b \quad , \quad (60)$$

and the total transition probability for ionization is expressed in terms of $V_{fi}(R,k)_{BF}$, which is a linear combination of interaction matrix elements of Equation (50):

$$V_{fi}(R,k)_{BF} = \sum_{a,b} C_b^* C_a V_{ba}(R,k)_{BF} \quad . \quad (61)$$

According to this general description, Equations (57) and (58) of the UA analysis may be applied using the ℓ value restrictions directly with values found from an MO correlation diagram such as in Figure 9a, but remembering that the m-value restrictions are weakened due to Born-Oppenheimer couplings.

Of course, ionization occurs far from the UA limit, and the values for ℓ_1' which are obtained here are certainly not all which should be included, but they do constitute the minimal set required for making a reasonable physical description of the emitted electron. That such a minimal set can be specified is important for the parameterization of expressions at various levels of approximation by which calculations of angular distributions of the emitted electrons can be made (Eb74, Mi75).

3. Estimating MO Correlation Diagrams for Diatomics

An analysis such as has just been outlined requires only schematic correlation diagrams, which should, however, be reliable in relating SA and UA limits of the higher lying MO's. In this section, a procedure will be described for estimating MO correlation diagrams, and applied to the collision pairs $\text{He}^*(1s2s) + \text{Ar}(3p^6)$, $+ \text{Kr}(4p^6)$, $+ \text{Hg}(6s^2)$, and $\text{Ne}^*(2p^53s) + \text{Ar}(3p^6)$. Based on these estimated MO correlation diagrams and the analysis of the previous section, the minimal set of angular momentum contributions required to describe the emitted electrons in PI and AI will then be determined.

In order to begin constructing estimated MO correlation diagrams, one must have the appropriate SA and UA atomic orbital energy levels of the collision partners both before and after ionization. The following scheme has been found to be sufficiently reliable and simple to apply. For the ground state levels of neutral atoms one can use any of the results of the Hartree-Fock or Hartree-Fock-Slater calculations, which are available in tabulated form in the literature (Fi73, De73, Ma67a, Cl74). Furthermore, one can rely on these calculated atomic orbital energy levels for ground state neutral atoms in order to obtain the levels of the ground and excited state atomic ions and of excited state neutral atoms. Clementi and Roetti

have published results of Hartree-Fock calculations on ground states of atomic ions as well as neutral atoms for $Z \leq 54$ (Cl74). Comparison of these results shows that the spacing between the levels of any two of the higher occupied orbitals of the neutral atoms is very nearly preserved for the corresponding two orbitals of the atomic ions. This observed property of the Hartree-Fock orbitals lends itself well to a quite accurate determination of the levels of ground state ions for all of the atoms. One simply locates the level of the highest occupied orbital at the ionization potential of the atomic ion in question, below which the next few levels are positioned according to their relative spacing in the corresponding neutral atom. Ionization potentials can be readily found, for example, in a CRC Handbook of Chemistry and Physics.

The levels of excited states of neutral atoms and atomic ions involve somewhat more uncertainty in their determination. The essential requirement these levels should satisfy is that of being properly ordered with respect to energy. Within an atomic orbital framework, basically two types of excited states may occur. First are the excited states formed from the ground state by promotion of an electron(s) from an inner shell to a higher level previously completely unoccupied in the ground state (such as $\text{Ca}(3p^6 4s^2) \rightarrow \text{Ca}^*(3p^5 4s^2 3d)$). Second are the excited states

formed from the ground state by promotion of an electron(s) from an inner shell to a higher level previously partially occupied in the ground state (such as $\text{Pb}(5d^{10}6s^26p^2) \rightarrow \text{Pb}^*(5d^96s^26p^3)$). In this second case, the excited state only involves altering the occupation numbers of orbitals already partially occupied in the ground state, and, though levels will be shifting due to this, it is expected that the levels of the excited state will be well described by those of the parent ground state. However, in the first case mentioned above, the promoted electron(s) can be treated as moving in the field of the remaining electrons in the ionic state characterized by the appropriate vacancy(s). Therefore, the ionic core levels are determined as previously described, and then a version of Slater's rules (Sl60), based on estimated screening factors, is applied to describe the level(s) of the promoted electron(s) in the presence of the ionic core.

The construction of the schematic MO correlation diagrams will now be discussed. In order to proceed, the following fundamental guidelines are followed:

- (a) Only those MO levels are considered which conform at the SA limit to given atomic orbital levels of either the reactant or product collision partners.
- (b) The MO levels, for both the excited molecule and the molecular ion, correlate from SA to UA limits in accordance with the non-crossing rule for spin-polarized orbitals.

The specific example of $\text{He}^*(1s2s) + \text{Ar}(3p^6)$ will show how these guidelines are applied. Referring to Figure 9a, on the right are displayed the occupied levels of $\text{He}^*(1s2s)$ and $\text{Ar}(3p^6)$, determined as described earlier in this section. It is pointed out that the procedure for estimating levels of excited atoms leaves some uncertainty as to effects of spin splittings. Normally, except for the high lying level of the promoted electron in an excited atom, splitting due to spin-polarization is expected to be small compared to the relative spacings of the levels. However, Helium in its $1s2s$ excited states is a rather special case since there are only two electrons. The estimates made here of the occupied $1s$ and $2s$ levels of excited Helium (based on estimated screening factors) are certainly reasonable, especially in relation to the $3s$ and $3p$ levels of $\text{Ar}(3p^6)$. But each of these occupied levels has associated with it the level of its unoccupied partner of opposite spin. The unoccupied $1s$ level of He^* may lie below or above the $3s$ level of $\text{Ar}(3p^6)$, depending on whether there is a weak or a strong splitting of the two $1s$ spin components (one occupied and one unoccupied). Applying the guidelines (a) and (b) to the case of weak splitting, one would find the SA levels correlating to UA levels of an excited state of Calcium denoted by $\text{Ca}^*(3s3p^6 4s^2 3d)$. That is, the unoccupied $1s$ level, lying below the $3s$ level

of $\text{Ar}(3p^6)$ and obeying the non-crossing rule, would go to the partially occupied $3s$ level of $\text{Ca}^*(3s3p^64s^23d)$. On the other hand, in the case of strong splitting, the SA levels correlate to UA levels of $\text{Ca}^*(3s^23p^54s^23d)$. That is, the unoccupied $1s$ level, lying above the $3s$ level of $\text{Ar}(3p^6)$, would go to the partially occupied $3p$ level of $\text{Ca}^*(3s^23p^54s^23d)$. The calculations reported earlier in this chapter confirm that, of the two estimated possibilities, this latter situation is the case. In Figure 9a is displayed the MO correlation diagram of the occupied MO's for this latter case, where the two spin components of the $\sigma 3s$ orbital branch, one approaching the UA $3s$ level and the other the UA $3p$ level, in the way required by the non-crossing rule and shown in Figure 8 for the calculated spin-polarized results.

As Figure 9a shows, the MO's are designated at the right and left according to their large R and small R behavior, respectively, and are labeled by their appropriate SA and UA atomic orbital limits. The convention used for these schematic MO correlation diagrams is to designate by a single line the levels of both spin components (α and β) of an orbital, except for situations where one spin component is occupied and the other unoccupied (such as $\sigma 1s(\alpha)$), or where the non-crossing rule requires that the two occupied spin components of a given orbital correlate each to

a different UA or SA atomic orbital (such as occurs for the $\sigma 3s(\alpha, \beta)$ levels).

It is emphasized that the $1s2s$ state of excited Helium really provides an extreme example of the effects of spin-splitting due to the fact that only two electrons are involved. The discussion of $\text{He}^*(1s2s) + \text{Ar}(3p^6)$ indicates that one could reasonably limit the possibilities to only two. With the additional effort of performing spin-polarized calculations of the $1s2s$ excited states of Helium, one then could resolve which of the two cases was applicable. Certainly calculations on SA and UA excited atoms lend themselves to a more definite estimation of MO correlation diagrams, but require a higher level of effort and would be helpful only for certain borderline cases.

Continuing now with the example of $\text{He}^*(1s2s) + \text{Ar}(3p^6)$, a determination is made of the various possible Auger processes which result in MO's for the molecular ion that correlate according to guidelines (a) and (b) to the correct SA atomic orbital levels of the product channel. In the notation of the previous section, u_1 will designate the $\sigma 2s$ orbital (or $\pi 2p$ orbital which shares the same UA $3d$ orbital limit), u_1' the continuum state of the emitted electron. u_2 can then possibly be $\sigma 3p$ or $\pi 3p$, which correlate, respectively, to UA $4s$ and $3p$ atomic orbitals as shown in Figure 9a. Therefore, if an electron in $\sigma 3p$ participates in the Auger process, the resulting UA atomic ion from

which the MO's separate in the product channel would be $\text{Ca}^+(3p^6 4s)$. A correlation diagram for $\text{He} + \text{Ar}^+$, where $\text{Ca}^+(3p^6 4s)$ is the UA ion, is not shown, but one may consult instead the correlation diagram for $\text{He} + \text{Kr}^+$ in Figure 10b, which will be discussed shortly, and which shows for the $\text{He}^* + \text{Kr}$ case the exactly analogous situation, where, in place of $\text{Ca}^+(3p^6 4s)$, $\text{Sr}^+(3p^6 5s)$ is the UA ion. Referring now to the right of Figure 9b, the occupied SA levels of ground state $\text{Ar}^+(3p^5)$ all lie below the doubly occupied $1s$ level of $\text{He}(1s^2)$. This has been confirmed by spin-polarized calculations on $\text{Ar}^+(3p^5, ^2P)$. Therefore, the level of the empty $4s$ spin component of UA $\text{Ca}^+(3p^6 4s)$, which is split above its occupied counterpart, could not correlate in the SA limit to the partially occupied $3p$ level of $\text{Ar}^+(3p^5)$ without violating the non-crossing rule with a spin component of the σ orbital which separates to the $1s$ level of $\text{He}(1s^2)$. Therefore, guidelines (a) and (b) do not favor an Auger process where u_2 is the $\sigma 3p$ orbital. On the other hand, if u_2 is the $\pi 3p$ orbital, then upon ionization the appropriate UA ion will be $[\text{Ca}^+](3p^5 4s^2)$, which is shown in Figure 9b, and from which the MO's do correlate to the atomic levels of $\text{He}(1s^2)$ and $\text{Ar}^+(3p^5)$ without violating guidelines (a) and (b). The analysis of the angular momentum contributions to the emitted electron is, therefore, performed on the basis of both Auger type processes, with the awareness, however, that guidelines (a) and (b)

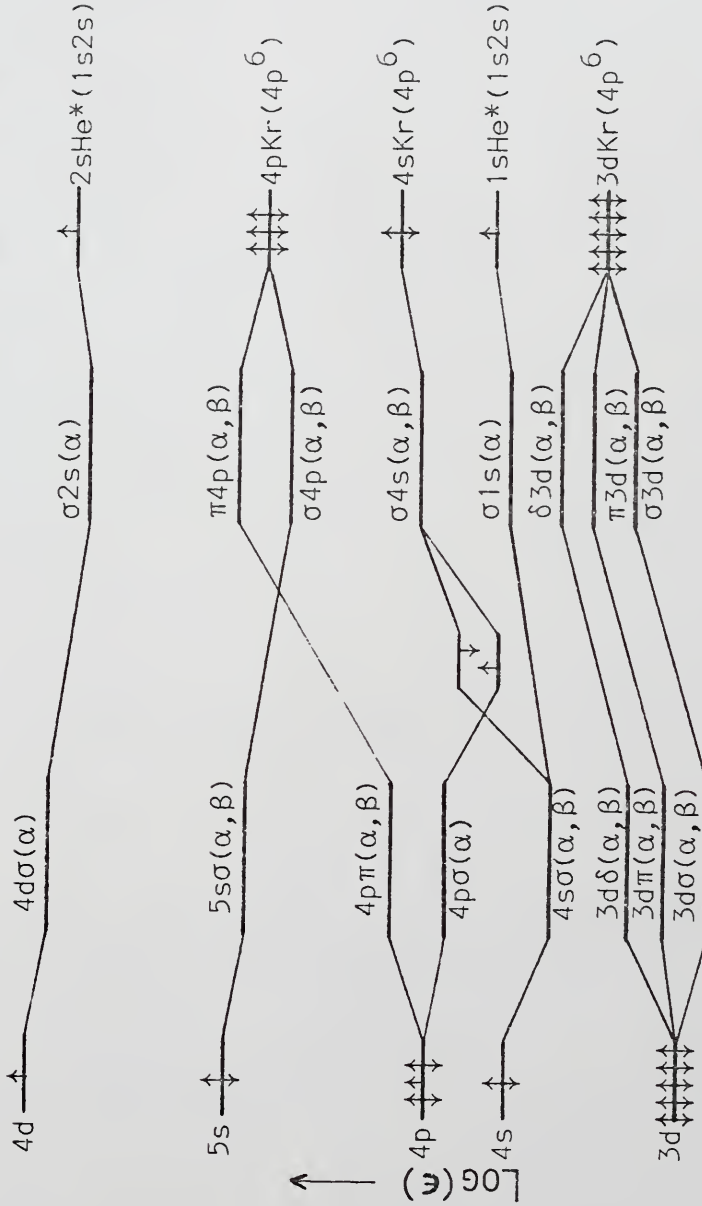
favor the one involving the $\pi 3p$ orbital.

This detailed discussion of the $\text{He}^*(1s2s) + \text{Ar}(3p^6)$ case demonstrates just how one goes about analyzing PI and AI processes in terms of estimated MO correlation diagrams. In Figures 10 to 12 the results of similar analyses, performed, respectively, on $\text{He}^*(1s2s) + \text{Kr}(4p^6)$, $+ \text{Hg}(6s^2)$, and $\text{Ne}^*(2p^5 3s) + \text{Ar}(3p^6)$, are shown.

Attention is drawn to the similarity between the results for excited Helium + Krypton of Figure 10a and those for excited Helium + Argon of Figure 9a. The MO's from the 4s and 4p levels of $\text{Kr}(4p^6)$ have near exact counterparts in those from the 3s and 3p levels of $\text{Ar}(3p^6)$. So, the unoccupied 1s level of $\text{He}^*(1s2s)$ is expected to lie above the 4s level of Kr. A comparison of Figures 10a and 9a suggests that $\text{He}^*(1s2s)$ in collision with $\text{Kr}(4p^6)$ goes through the same Auger type processes as it does in collision with $\text{Ar}(3p^6)$. However, in Figure 10b one sees that the SA 4p level of $\text{Kr}^+(4p^5)$ lies very close to the 1s level of $\text{He}(1s^2)$, enough so that the splitting of the spin components of the $4p\text{Kr}^+$ level could likely result in the level of the partially occupied component lying above the 1sHe level. If it lies above, then the Auger type process favored for Kr would be different from that for Ar, and would permit the MO correlation diagram for $\text{He} + \text{Kr}^+$ shown in Figure 10b; if it lies below, then the Auger type process favored for Kr would cor-

Figure 10a. Estimated molecular orbital correlation diagram for $\text{He}^*(1s2s) + \text{Kr}(4p^6)$.

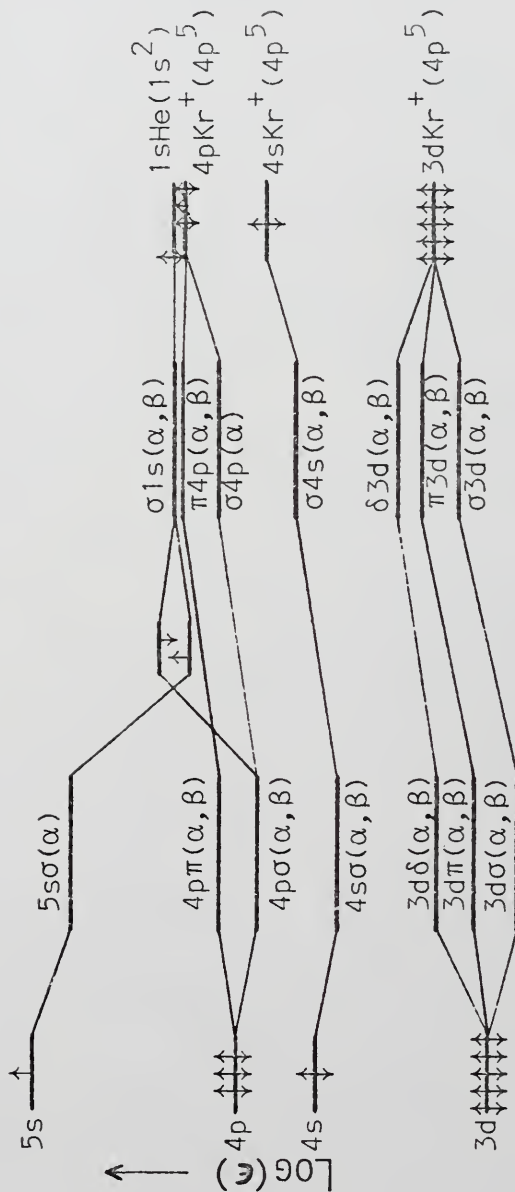
$\text{He}^* - \text{Kr} \quad (\alpha)$



$\text{Sr}^*(4p^5 5s^2 4d)$

Figure 10b. Estimated molecular orbital correlation diagram for $\text{He}(1s^2) + \text{Kr}^+(4p^5)$.

He-Kr⁺ (b)



$R \longrightarrow$

$\text{Sr}^+(4p^6 5s)$

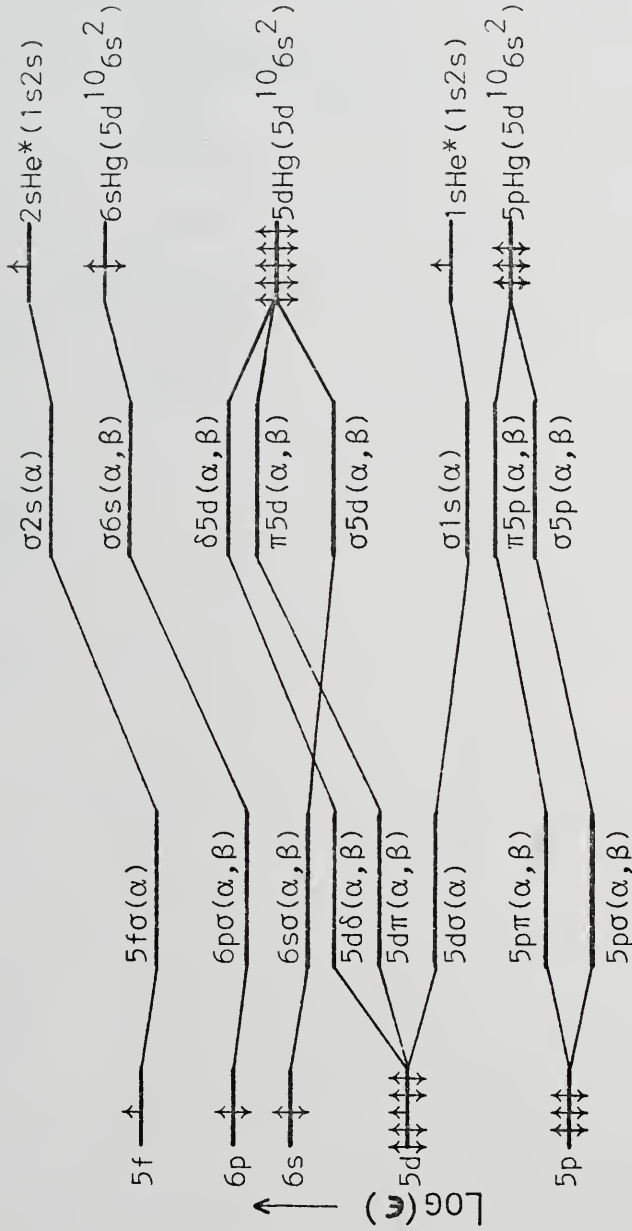
respond to the one we found favored for Ar, and would permit an MO correlation diagram for $\text{He} + \text{Kr}^+$ analogous to the one shown for $\text{He} + \text{Ar}^+$ in Figure 9b. Considering its borderline nature, the analysis of the angular momentum contributions to the emitted electron shall be made in both these cases for $\text{He}^*(1s2s) + \text{Kr}(4p^6)$.

The MO correlation diagram for $\text{He}^*(1s2s) + \text{Hg}(6s^2)$ shown in Figure 11a is the one which applies if the level of the unoccupied $1s$ spin component of $\text{He}^*(1s2s)$ lies below the $5d$ level of ground state Hg. Auger processes involving $\delta 5d$, $\pi 5d$, or $\sigma 5d$ MO's can be ruled out, and Figure 11b shows the MO correlation diagram for the molecular ion for an Auger process involving the $\sigma 6s\text{Hg}$ MO, in terms of which the analysis of the angular momentum components of the emitted electron is carried out.

Only σ and π orbitals are occupied in the SA limit of $\text{Ne}^* + \text{Ar}$, as seen in Figure 12a. This means no more than six electrons can correlate to the $3d$ orbital of the UA excited state of Ni. As a result, a very highly excited state of Ni results at the UA limit. Shown in Figure 12a is the case of the $\pi 2p\text{Ne}^*$ MO filled and the $\sigma 2p\text{Ne}^*$ MO partially filled, corresponding to a $1,^3\Sigma$ molecular state. Also to be considered is the case of the $\pi 2p$ MO partially occupied and the $\sigma 2p$ MO filled, corresponding to a $1,^3\Pi$ molecular state and resulting in an excited state of UA

Figure 11a. Estimated molecular orbital correlation diagram for $\text{He}^*(1s2s) + \text{Hg}(6s^2)$.

He* - Hg (a)

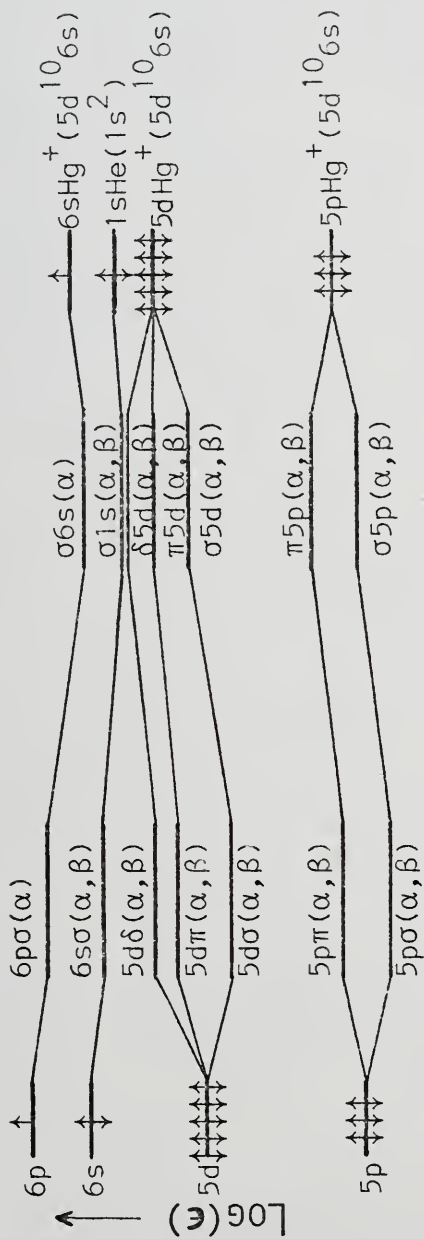


$R \longrightarrow$

$Pb^*(5d^9 6s^2 6p^2 5f)$

Figure 11b. Estimated molecular orbital correlation diagram for $\text{He}(1s^2) + \text{Hg}^+(6s)$.

He - Hg⁺ (b)



R →

Pb⁺ (5d¹⁰ 6s² 6p)

Figure 12a. Estimated molecular orbital correlation diagram for $\text{Ne}^*(2p53s) + \text{Ar}(3p6)$.

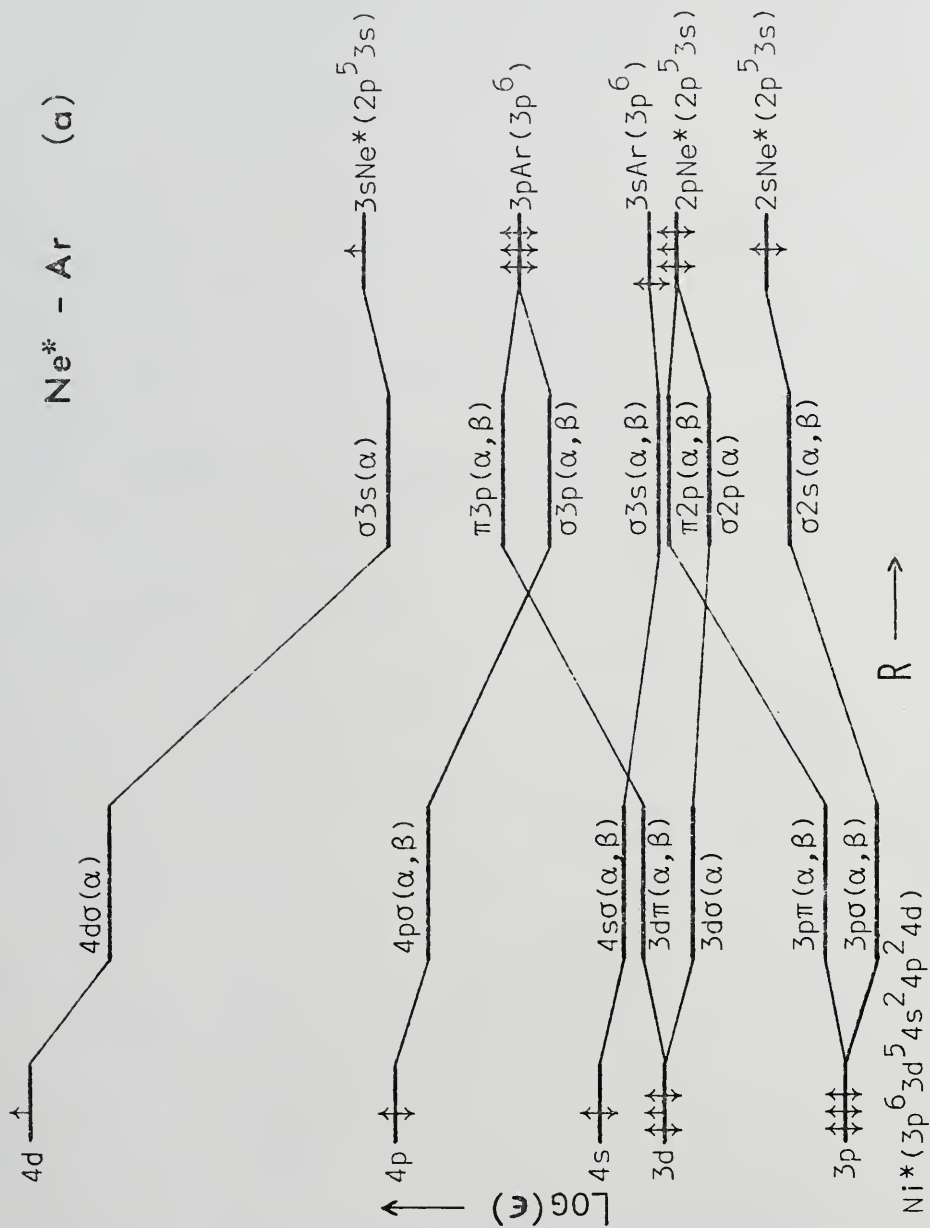
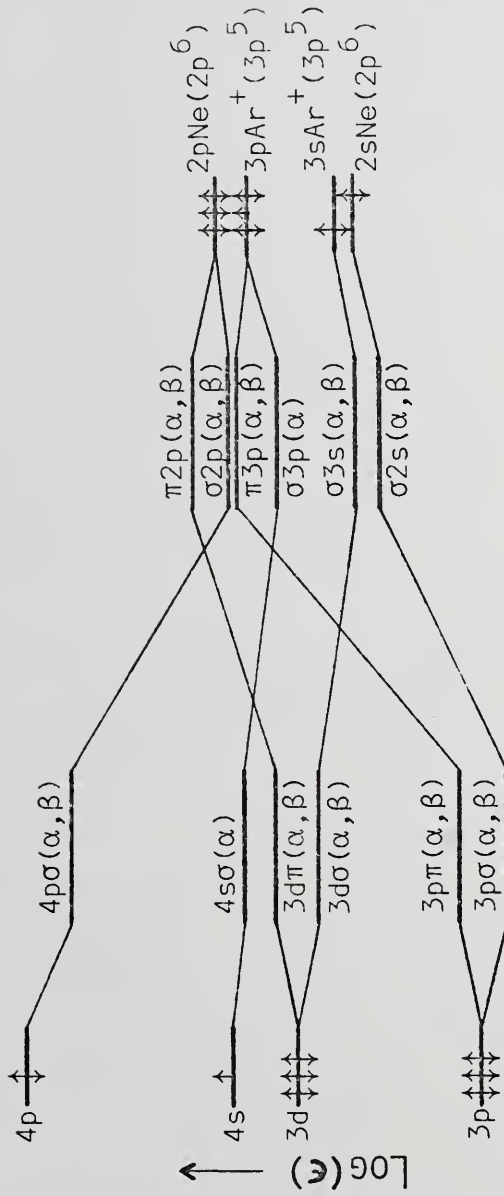


Figure 12b. Estimated molecular orbital correlation diagram for $\text{Ne}(2p^6) + \text{Ar}^+(3p^5)$.

Ne - Ar⁺ (b)



$[Ni^+]^*(3p^6 3d^6 4s 4p^2)$ $R \longrightarrow$

Ni denoted by $\text{Ni}^*(3p^5 3d^6 4s^2 4p^2 4d)$. Auger processes involving $\sigma 3p$ and $\pi 3p$ MO's can be ruled out, whereas those involving the $\sigma 3s$ MO are allowed, resulting in the MO correlation diagram for the molecular ion shown in Figure 12b. This analysis assumes that the levels of both spin components of the $2p$ orbital of $\text{Ne}^*(2p^5 3s)$ lie below the $3s$ level of ground state Ar, which, according to Figure 12a, is not unreasonable.

On the basis of the MO correlation diagrams presented in Figures 9 to 12, together with the analysis of the previous section, an evaluation of the minimal set of angular momentum contributions needed in describing the emitted electrons is made. These results for the various PI and AI processes are shown in Table II. The ℓ values for $\text{He}^* + \text{Ar}$ and $\text{He}^* + \text{Kr}$ are tabulated according to which of the two previously discussed cases they belong. The favored case for $\text{He}^* + \text{Ar}$, which is supported by the spin-polarized atomic calculations, is indicated. Because of the borderline nature of the $\text{He}^* + \text{Kr}$ estimates, both cases should be equally considered within this analysis.

A feature common to all of the collision pairs studied is that relatively few angular momentum components are predicted as being necessary to reliably represent the angular behavior of the emitted electrons in the BF frame. This result lends additional support to existing evidence that few partial waves need be kept when calculating electron

Table II. Minimal set of angular momentum components in the body-fixed frame predicted for electrons emitted in PI and AI collisions

Collision Pairs	Predicted ℓ Values
He* + Ar	0, 2, 4 (favored) 1, 3
He* + Kr	0, 2, 4 1, 3
He* + Hg	0, 2, 4, 6
Ne* + Ar	0, 1, 2, 3, 4

angular distributions, which confirms experimental measurements (Eb74, Mi75). As can be seen, $\text{He}^* + \text{Hg}$ involves only even values of ℓ , indicating an angular distribution of emitted electrons symmetric about 90° in the BF frame. It should be pointed out that in all cases the ℓ value analyses in terms of the direct and exchange matrix elements of Equation (55) give identical results, so that both couplings must be equally considered in MO descriptions.

4. Discussion

For the most part, the importance of MO correlation diagrams in understanding atomic collision processes has centered around the occurrence of crossings between MO eigen-energies which are associated with electron promotion mechanisms for electronic excitation or charge transfer (see, for instance, Ba72, Li67 and Ke74). In the present chapter, quite another application of MO correlation diagrams has been made. The model and calculated results correspond to a mechanism of ionization in PI and AI collisions associated with an Auger type process, rather than one associated with electron promotion.

In the analysis of this chapter, the MO's obey the non-crossing rule for spin-polarized orbitals. However, the reliance upon adiabatic spin-polarized MO's is not to

be confused with the fact that the total system of electrons is represented by diabatic states constructed as determinants of the MO's, either before or after ionization. Therefore, coupling between these states derives from Coulomb as well as Born-Oppenheimer terms, as discussed in Chapter I.

The work reported in this chapter has been prompted by that of Micha and Nakamura (Mi75). The two approaches lead to results which confirm one another, while at the same time they each emphasize a different point of view. Micha and Nakamura also consider adiabatic MO's, but inherent in their approach is to assume that the MO from which the emitted electron escapes has associated with it a width (or decay rate) for leakage into the continuum. There, the UA analysis of the angular momentum contributions to the emitted electron in the BF frame follows according to rules for auto-ionization. In the approach of the present chapter, emphasis is placed on the Auger type process, and the UA analysis of the angular momentum contributions to the emitted electrons focuses on the direct and exchange matrix elements of the Coulomb coupling, with equal importance placed on both. Also, owing to its R^{-2} dependence, rotational Born-Oppenheimer coupling is found to be significant for properly assessing all of the angular momentum contributions. Such rotational Born-Oppenheimer

coupling is of particular importance when the two MO's, by which two initial or final determinantal wave functions differ, share the same UA atomic orbital limit.

In the present analysis, useful application has been made of estimated MO correlation diagrams. The estimated correlation diagrams themselves rely upon estimated atomic orbital energy levels for atomic ions and excited atoms. The procedure proposed for estimating levels of occupied atomic orbitals in atomic ions and excited atoms appears to be quite reliable, and requires only tabulated results for ground state atoms together with an application of Slater's rules based on estimated screening factors. However, uncertainty remains in the atomic level estimates in connection with splitting due to spin-polarization. With the additional effort involved in carrying out spin-polarized calculations on atomic ions and excited atoms, much of this uncertainty could be avoided, which would lead to even more reliable MO correlation diagrams.

Nevertheless, the convenience of estimated MO correlation diagrams based on estimated atomic levels, and requiring no large scale calculations, makes possible ready application to a variety of collision partners. On the basis of the estimated MO correlation diagrams, together with the two mentioned fundamental guidelines, just a few of the several possible Auger processes may be singled out as

being important. In this connection, the diagrams for the molecular ion of the product channel are seen to play a necessary role.

CHAPTER IV

A COUPLED CHANNELS APPROACH TO PENNING IONIZATION OF Ar BY $\text{He}^*(1s2s, {}^3S)$

Having dealt in the previous two chapters with matters specifically related to electronic structure during the course of a collision between two atoms, the focus of attention is now turned to the collision dynamics of the heavy particles (nuclei). The particular case of PI of Ar by $\text{He}^*(1s2s, {}^3S)$ will be considered in detail, and calculations of total and partial ionization cross-sections will be reported.

In order to properly describe the heavy particle motion during a process such as PI, one must keep in mind that initially, before ionization, the internal electronic state of the diatom is a discrete (metastable) state which is embedded in a continuum of internal electronic states associated with the free emitted electron together with the remaining bound $N-1$ electrons after ionization. These features have been mentioned previously in this dissertation. So the first concern of this chapter will be to augment the formal development of Chapter I to include continuum as well as discrete electronic states in the expansion of Equation (26).

Next, following an approach applied by Wolken (Wo75) to collisional dissociation of diatomic molecules by atoms, the continuum coupled equations will be discretized, resulting in a set of modified coupled equations analogous to Equation (34). Similar discretization techniques have been employed in connection with nuclear reactions, as described in the work of Bloch (Bl66). The procedure for solving the modified coupled equations with scattering boundary conditions will be presented, pointing out the pertinent quantities for calculating partial and total cross-sections.

Next a qualitative discussion of the important features of PI and AI will be presented, followed by an application of a discretization procedure to these processes, which entails an approximation of the set of coupled equations in terms of several two-channel coupled equations. The specifics of the actual calculations of PI of Ar by $\text{He}^*(1s2s, {}^3S)$ will then be presented. Convenient functional forms are used to describe the interaction potentials associated, respectively, with the excited (metastable) state of the He-Ar molecule in the initial channel, and the ground state of the $(\text{He-Ar})^+$ molecular ion in the product channel. The parameters used in these potential functions are discussed in terms of the behaviors of the potentials in the crucial regions of short range repulsion, long range attraction, and near the potential minimum.

Based upon functional forms for the "width", or decay rate into the continuum, which have been suggested in semi-empirical approaches to PI and AI, it is possible to extract equally useful expressions for the coupling between the incident and product channels.

Finally the results of the coupled channels calculations for PI in $\text{He}^*(1s2s, {}^3S) + \text{Ar}(3p^6)$ collisions are presented and discussed.

1. The Scattering Problem in Terms of Discrete and Continuum Electronic States

In the formal development of Chapter I, coupled equations, determining the heavy particle motion during a collision between two atoms, were derived by appropriately expressing the Hamiltonian and wave function for the nuclei and electrons in independent variables in the BF-CMN frame, and then introducing an expansion in terms of a complete set of electronic wave functions at each internuclear separation, R , according to Equation (26). Although not explicitly stated in Chapter I, the treatment in terms of Equation (26) is carried out under conditions of a discrete basis set of electronic wave functions. Of course, a complete description of any system of electrons would include both the discrete as well as continuum parts of the spectrum. However, many inelastic collisional processes involve primarily transitions between bound electronic states (such as excitation or charge transfer) or transfer

of energy from bound electronic states to motion of the heavy particles (such as electronic to translational or vibrational energy transfer). So in practice, for these processes only a discrete set of electronic states need be considered.

On the other hand, collisional ionization processes require of necessity that both discrete as well as continuum electronic states be included in representing the so-called internal states of the system during collision. To set the stage for the specific treatment in this chapter of the dynamics of the heavy particle motion in PI of Argon by metastable Helium, the formal development of Chapter I will be extended to include both discrete and continuum electronic states.

Keeping in mind PI processes, the continuum electronic states which will be considered are those associated with an electron escaping the region of the molecule along a direction specified by the unit vector $\hat{e}$ (in the BF frame), and having kinetic energy ϵ which is constrained by conservation of total energy during the collision. Physically, once ionization has occurred, the system of N electrons consists of the emitted electron (of energy ϵ and direction $\hat{e}$) in the presence of the remaining $N-1$ electrons in some state of the molecular ion. The continuum state of the emitted electron can therefore be well represented by an appropriate linear combination of Coulomb wave functions.

Designating the continuum state of the emitted electron by $u_{\epsilon, \hat{e}}^C(\vec{r})$, one can write (see, for instance, Ku75)

$$u_{\epsilon, \hat{e}}^C(\vec{r}) = \sum_{\ell m} Y_{\ell m}^*(\hat{e}) u_{\epsilon \ell m}^C(\vec{r}) , \quad (62)$$

where $u_{\epsilon \ell m}^C(\vec{r})$ is a Coulomb wave function of energy ϵ with angular momentum partial wave values ℓ and m in the BF frame. That is (see, for instance, Be57),

$$u_{\epsilon \ell m}^C(\vec{r}) = \frac{1}{r} R_{\epsilon \ell}(r) Y_{\ell m}(\hat{r}) . \quad (63)$$

The work of the previous chapter centered around an analysis, in terms of molecular orbital correlation diagrams, of the minimum number of such partial wave contributions required to describe the emitted electron in the BF frame. The asymptotic behavior of the radial function, $R_{\epsilon \ell}(r)$, in Equation (63) is

$$R_{\epsilon \ell}(r) \underset{r \rightarrow \infty}{\sim} \sqrt{\frac{2}{\pi k}} \frac{\sin(kr + \delta_{\ell} + \sigma_{\ell} - \frac{\ell\pi}{2} + \frac{1}{k} \ln(2kr))}{r} , \quad (64)$$

where $k = \sqrt{2\epsilon}$ is the wave number in atomic units, σ_{ℓ} is the Coulomb phase shift of the ℓ^{th} Coulomb partial wave, and δ_{ℓ} is the phase shift arising from the actual physical situation. Reference will be made later on in this chapter to Equation (64).

The continuum orbitals of Equation (62) are normalized to unity on the energy scale. By this is meant the following:

$$\langle u_{\epsilon, \hat{e}}^C | u_{\epsilon', \hat{e}'}^C \rangle = \int d\vec{r} u_{\epsilon, \hat{e}}^{C*}(\vec{r}) u_{\epsilon', \hat{e}'}^C(\vec{r}) = \delta(\epsilon - \epsilon') \delta(\hat{e} - \hat{e}'). \quad (65)$$

A good discussion of the normalization of continuum wave functions has been given by Bethe and Salpeter (Be57). Confusion can easily arise regarding the normalization of continuum functions. In this work, the expression, "normalized to unity on the energy scale", will be used, and it will refer to normalization according to Equation (65). It is worth noting that continuum functions have units which differ from their bound function counterparts. That is, if a set of bound (normalized) functions, $\{u_i\}$, are orthonormal, $\langle u_i | u_j \rangle = \delta_{ij}$ is unitless, whereas, for continuum functions (normalized to unity on the energy scale), $\langle u_\epsilon | u_{\epsilon'} \rangle = \delta(\epsilon - \epsilon')$ has units of $(\text{energy})^{-1}$ (as is readily seen since $\int d\epsilon \delta(\epsilon - \epsilon') = 1$). Therefore, in the case of normalization to unity on the energy scale, the units of a continuum function will differ from those of a bound function by $(\text{energy})^{-1/2}$.

The generalization of the coupled equations of Chapter I in terms of discrete and continuum electronic states proceeds straightforwardly. One formally augments the orthonormal basis of discrete electronic states, $\{\phi_{n\Lambda}\}$, with a complete set of continuum electronic states, $\{\phi_{\eta\Lambda}\}$, which are orthogonal to the discrete set. Here, the continuum variable, η , refers to the energy, ϵ , as well as the angular momentum partial wave values in the BF frame, ℓ and m . That is, $\eta = (\epsilon \ell m)$. In other words, the continuum

electronic states introduced are those associated with a particular partial wave component of the emitted electron in the BF frame. Therefore, the Λ label of the continuum electronic states designates the component of angular momentum of the electrons along the internuclear axis associated with the (ℓm) partial wave of the emitted electron and the remaining $N-1$ bound electrons in a state with axial component of angular momentum, Λ_+ . That is, $\Lambda = m + \Lambda_+$. The normalization conditions are taken as follows:

$$\langle \phi_{n\Lambda} | \phi_{n'\Lambda'} \rangle = \delta_{nn'} \delta_{\Lambda\Lambda'}$$

$$\langle \phi_{n\Lambda} | \phi_{\eta\Lambda} \rangle = \langle \phi_{n\Lambda} | \phi_{\eta\Lambda'} \rangle = 0$$

$$\langle \phi_{\eta\Lambda} | \phi_{\eta'\Lambda'} \rangle = \delta(\eta - \eta') \delta_{\Lambda\Lambda'} \quad . \quad (66)$$

Here, $\delta(\eta - \eta') = \delta(\epsilon - \epsilon') \delta_{\ell, \ell'} \delta_{m, m'}$.

Again, as in Chapter I, the discrete and continuum states introduced here have been left quite general, aside from the normalization conditions of Equation (66). In practice, however, N electron states constructed as determinants of one-electron molecular orbitals constitute convenient and useful basis wave functions for both discrete and continuum states, as has been emphasized in Chapters II and III. Accordingly, the discrete electronic states can be described in the limited configuration space spanned by determinantal wave functions comprised of bound (normalized) one-electron molecular orbitals, and the

continuum electronic states can be described in the limited configuration space spanned by determinantal wave functions formed from $N-1$ bound (normalized) one-electron molecular orbitals together with a continuum orbital such as in Equation (63), normalized to unity on the energy scale and orthogonal to the bound molecular orbitals (see, for instance, Bl66). This chapter continues in the context of such diabatic representations, as discussed in the previous chapters, and applied to both the discrete and continuum electronic states.

Before deriving a continuously infinite set of coupled equations for scattering involving discrete and continuum electronic states, some remarks, pertinent to the conditions under which collisional processes take place, should be made, especially in order to maintain continuity with the formal development of Chapter I. In Chapter I, attention was focused on a total wave function for the system of electrons and nuclei prepared in a specific eigenstate of the square of the total angular momentum, $\vec{K} = \vec{L}^{(n)} + \vec{L}^{(e)}$, and its z (SF frame) component (see Equations (6) and (23)). In other words, the wave function of Equations (6) or (23) describes the electrons and nuclei where the electronic and nuclear angular momenta are coupled in such a way that their state is an eigenfunction of K^2 and K_z with eigenvalues $K(K+1)$ and M , respectively. However, the conditions of an actual collision process are specified by the

asymptotic boundary conditions of the incident and final channels. The colliding atoms are characterized ideally by their relative translational momentum and the internal electronic states in which they have been prepared. Before collision, the electronic states of the two atoms are essentially unperturbed atomic states, and the electrons of each atom together have some total angular momentum and component along the (asymptotic) internuclear axis (which may or may not correspond to the SF-CMN z axis). A description of the incident relative translational momentum prepared for the two atoms involves a linear combination over all angular momentum partial waves (eigenvalues of $(L^{(n)})^2$ and $L_z^{(n)}$) of the nuclei. Before collision, the electronic angular momentum of each atom together with the nuclear angular momentum are all uncoupled, and for each partial wave of the nuclear motion, the three combined result in a total angular momentum and z component contribution prior to collision. All partial waves of the nuclear motion are required to describe the relative motion of the two atoms before collision. Consequently, all possible values of the total (nuclear and electronic) orbital angular momenta and z components must be properly included in establishing the coupled equations for the heavy particle motion. That is, as the two atoms collide, the electronic structure of the resulting diatom is determined by molecular states appropriately built from the two

atomic states, and characterized by an electronic angular momentum with some component, Λ , along the internuclear axis. This molecular electronic angular momentum couples with the angular momentum partial waves of the nuclear motion resulting in all possible values of the total angular momentum and its z component, (KM). To each of these partial waves is associated a contribution in accordance with the appropriate angular momentum vector coupling coefficients.

So, strictly speaking, the development of Chapter I constitutes only a starting point for a more complete treatment of the coupled equations, which would include all of the required coupling of electronic and nuclear angular momenta. However, by considering a particular partial wave component of the total orbital angular momentum during collision, the development of Chapter I establishes how the Schrödinger equation can be properly expressed in the BF-CMN frame, involving electronic wave functions and coupling matrix elements calculated in the BF-CMN frame.

In the actual application to PI of $\text{Ar}(3p^6, ^1S)$ by $\text{He}^*(1s2s, ^3S)$, which will be eventually presented in this chapter, the colliding atoms give rise to only a $^3\Sigma$ molecular term. Therefore, the electronic angular momentum in the incident channel is very small compared to the angular momentum of the nuclei, which typically has values

around 15 or 20. So only the nuclear angular momentum has to be considered in the incident channel. Upon ionization, the emitted electron escapes with BF angular momentum components (ℓm), leaving the molecular ion in a $^2\Sigma$ or $^2\Pi$ state. The product Argon ion is in its ^2P ground state. In the previous chapter, the analysis of the BF angular momentum components of the emitted electron indicated that only few partial waves contribute. This confirms other such analyses (Eb74, Mi75), and according to the calculations of Micha and Nakamura (Mi75), the emitted electrons are predominantly in $\ell = 0$ states, with proportionately smaller contributions from the next few partial waves accounting for the anisotropy in their angular distributions (Ho71, Eb74 and Ni73). So, not only in the incident channel, but also in the product channel, the electronic angular momentum may be neglected in PI of Argon by metastable Helium.

Therefore, the details of electronic and nuclear angular momentum coupling in deriving the coupled equations will not be dealt with here. However, as a reminder of the fact that angular momentum coupling is important for a general treatment of the coupled equations, appropriate notation will be suggested, even though a complete analysis has not been carried out. It will be recognized, for instance, that the wave function of Equation (26) corresponds actually to a situation where the two atoms

are initially prepared in atomic states which result in initial molecular states labeled $(n_i \Lambda_i)$. Furthermore, for instance, the (KM) on the wave function of Equation (26) labels it as one of the contributing partial waves resulting from coupling of electronic and nuclear angular momentum partial waves in the SF frame, $(L_n M_n, L_e M_e)$, respectively. To the (KM) should be added the labels of the nuclear and electronic angular momenta which have coupled to constitute the (KM) partial wave. Accordingly, the index $\lambda = (L_n, L_e)$ will be introduced. In the case of a channel associated with a continuum electronic state, it is understood that $\vec{L}_e = \vec{L}_e^{(+)} + \vec{\ell}$, that is, the sum of the electronic angular momentum of the remaining ion and that of the emitted electron. Based on the preceding discussion, $L_e \ll L_n$ and $\ell \ll L_n$ for the actual application which will be carried out in this chapter.

The foregoing remarks have been made only to highlight some additional considerations regarding atom-atom collisions which are needed to place the formal development of Chapter I in perspective. Such details will not be needed in the application to PI of Argon by metastable Helium in this chapter. Serving as a guideline, however, the notation introduced here points to what may be expected from a more detailed analysis of electronic and nuclear angular momentum coupling.

Returning now to the primary consideration of this

chapter, in place of Equation (26) the partial contribution to the total wave function of nuclei and electrons is expanded in terms of discrete and continuum electronic states as follows:

$$\begin{aligned} \psi_{n_i \Lambda_i \lambda}^{KM}(R \theta \phi \vec{r}_i) &= (1/R) \sum_{\Lambda \lambda'} D_{M, \Lambda}^K(\phi \theta \gamma) \\ &\times \left\{ \sum_n \phi_{n \Lambda}(R, \vec{r}_i) \psi_{n \Lambda \lambda', n_i \Lambda_i \lambda}^{KM}(R) + \int_0^\infty d\epsilon \phi_{\eta \Lambda}(R, \vec{r}_i) \psi_{\epsilon \Lambda \lambda', n_i \Lambda_i \lambda}^{KM}(R) \right\}. \end{aligned} \quad (67)$$

The variables are understood to be the independent set in the BF-CMN frame discussed in Chapter I, and the tilde and primes designating, respectively, BF-CMN functions and variables in Chapter I, are omitted in this chapter. On the left of Equation (67), the partial contribution to the total wave function is labeled according to the molecular electronic state of the incident channel, $n_i \Lambda_i$, and corresponds to one of the possible couplings of electronic and nuclear angular momentum, designated by $KM\lambda$. The expansion coefficients, $\psi_{n \Lambda \lambda', n_i \Lambda_i \lambda}^{KM}$ and $\psi_{\epsilon \Lambda \lambda', n_i \Lambda_i \lambda}^{KM}$, specify the behavior of the heavy particles at each R associated with transition during collision from the $(KM\lambda)$ component of the initial channel, $n_i \Lambda_i$, to the $(KM\lambda')$ component of some other accessible channel, $n \Lambda$ or $\eta \Lambda$, respectively. It should be noted that the (ℓm) indices of $\eta = (\epsilon \ell m)$ are absorbed in the $(KM\lambda)$ indices of $\psi_{\epsilon \Lambda \lambda', n_i \Lambda_i \lambda}^{KM}$. As noted earlier in this chapter, the units

of the continuum states differ from those of the discrete states by $(\text{energy})^{-1/2}$. Referring to the expansion of Equation (67), one can see that a similar difference in units exists between the $\psi_{\varepsilon\Lambda\lambda', n_i\Lambda_i\lambda}^{\text{KM}}$ and the $\psi_{n\Lambda\lambda', n_i\Lambda_i\lambda}^{\text{KM}}$.

The coupled equations satisfied by the heavy particle wave functions, $\psi_{n\Lambda\lambda', n_i\Lambda_i\lambda}^{\text{KM}}$ and $\psi_{\varepsilon\Lambda\lambda', n_i\Lambda_i\lambda}^{\text{KM}}$, of Equation (67), are obtained essentially in the same way Equation (34) of Chapter I was obtained. By left multiplication of the Schrödinger equation (BF Hamiltonian of Equation (32) and wave function of Equation (67)) by $D_{M,\Lambda}^{K*}(\phi\theta\gamma)\psi_{n'\Lambda', n\Lambda}^*$ and integration over $(\phi, \theta, \gamma, \vec{r}_i)$, one finds

$$\begin{aligned} & \{ (1/2m) d^2/dR^2 - K(K+1)/2mR^2 + E \} \psi_{n'\Lambda', n\Lambda}^{\text{KM}}(R) \\ &= \sum_{\Lambda\lambda'} \left\{ \left[V_{n'\Lambda', n\Lambda}^{\text{Coul}}(R) + V_{n'\Lambda', n\Lambda}^{\text{BO}}(R) \right] \psi_{n\Lambda\lambda', n_i\Lambda_i\lambda}^{\text{KM}} \right. \\ &+ \left. \int_0^\infty d\varepsilon \left\{ V_{n'\Lambda', n\Lambda}^{\text{Coul}}(R) + V_{n'\Lambda', n\Lambda}^{\text{BO}}(R) \right\} \psi_{\varepsilon\Lambda\lambda', n_i\Lambda_i\lambda}^{\text{KM}}(R) \right\}. \end{aligned} \quad (68)$$

Here, for convenience, the Coulomb and Born-Oppenheimer couplings discussed in Chapter I have been introduced as follows:

$$V_{n'\Lambda', n\Lambda}^{\text{Coul}}(R) = \delta_{\Lambda', \Lambda} \langle \phi_{n'\Lambda'} | H_{\text{el}} | \phi_{n\Lambda} \rangle, \quad (69)$$

and

$$V_{n'\Lambda', n\Lambda}^{BO}(R) = V_{n'\Lambda', n\Lambda}^{rad}(R) + V_{n'\Lambda', n\Lambda}^{rot}(R) \quad , \quad (70)$$

where

$$V_{n'\Lambda', n\Lambda}^{rad}(R) = \delta_{\Lambda', \Lambda} \langle \phi_{n'\Lambda'} | - (1/m) d/dR - (1/2m) d^2/dR^2 | \phi_{n\Lambda} \rangle \quad , \quad (71)$$

and (referring to Equations (35) and (36) of Chapter I)

$$\begin{aligned} V_{n'\Lambda', n\Lambda}^{rot}(R) = & \delta_{\Lambda', \Lambda} \langle \phi_{n'\Lambda'} | (L^{(e)})^2 / 2mR^2 | \phi_{n\Lambda} \rangle \\ & - \delta_{\Lambda', \Lambda} \delta_{n', n} \Lambda^2 / mR^2 \\ & + \delta_{\Lambda', \Lambda+1} g_{\Lambda'\Lambda}^{KM+} \langle \phi_{n'\Lambda'} | L_+^{(e)} / 2mR^2 | \phi_{n\Lambda} \rangle \\ & + \delta_{\Lambda', \Lambda-1} g_{\Lambda'\Lambda}^{KM-} \langle \phi_{n'\Lambda'} | L_-^{(e)} / 2mR^2 | \phi_{n\Lambda} \rangle \end{aligned} \quad (72)$$

are the radial and rotational Born-Oppenheimer coupling contributions. Expressions similar to Equations (69), (70), (71) and (72) hold when the discrete labels, n' or n , or both n' and n , are replaced by continuum variable counterparts, η and η' . In Equations (69), (71) and (72), attention is drawn to the $\delta_{\Lambda', \Lambda}$ and $\delta_{\Lambda', \Lambda \pm 1}$ factors, which, though not seen explicitly in Equation (68), are important for assessing which electronic states enter the coupled equations due to Coulomb and Born-Oppenheimer couplings.

In similar fashion, multiplication of the Schrödinger equation on the left by $D_{M, \Lambda}^{K*}(\phi\theta\gamma) \phi_{\eta'\Lambda'}^*(R, \vec{r}_i)$ followed by

integration over $(\phi, \theta, \gamma, \vec{r}_1)$ leads to the resulting coupled equations:

$$\begin{aligned} & \{ (1/2m) d^2/dR^2 - K(K+1)/2mR^2 + E \} \psi_{\epsilon \Lambda \lambda', n_i \Lambda_i \lambda}^{KM}(R) \\ &= \sum_{\Lambda \lambda'} \left(\sum_n \{ V_{\eta \Lambda' \Lambda, n \Lambda}^{\text{Coul}}(R) + V_{\eta \Lambda' \Lambda, n \Lambda}^{\text{BO}}(R) \} \psi_{n \Lambda \lambda', n_i \Lambda_i \lambda}^{KM}(R) \right. \\ &+ \left. \int_0^\infty d\epsilon \{ V_{\eta \Lambda' \Lambda, n \Lambda}^{\text{Coul}}(R) + V_{\eta \Lambda' \Lambda, n \Lambda}^{\text{BO}}(R) \} \psi_{\epsilon \Lambda \lambda', n_i \Lambda_i \lambda}^{KM}(R) \right) \quad (73) \end{aligned}$$

Equations (68) and (73) formally constitute the coupled equations which determine the heavy particle motion associated with both discrete and continuum internal electronic states in atom-atom collisions.

2. Discretization of the Continuum and the Modified Coupled Equations

In order for the coupled equations of Equations (68) and (73) to be of any practical use, not only must the discrete set of electronic states (which in principle is infinite) be described in terms of relatively few, important, electronic states, but also the continuum electronic states must be treated in some manageable fashion. The terms involving integration over the energy, ϵ , of the emitted electron, which correspond to internal state couplings of the bound-continuum and continuum-continuum type, mean that Equations (68) and (73) constitute

a continuously infinite set of coupled equations which must be suitably reduced to some tractable form (see, for example, Bl66, Wo74 and Wo75). This may be accomplished by means of a discretization of the continuum with respect to the coupled equations of Equations (68) and (73).

The approach to discretization used here follows the work of Wolken in connection with gas-solid energy transfer (Wo74) and collision induced dissociation in atom-diatomic molecule scattering (Wo75), as well as that of Bloch (Bl66) in connection with nuclear reactions. The heavy particle wave functions associated with transitions into the continuum are formally expanded in a complete set of discrete functions of the continuum variable, ϵ :

$$\psi_{\epsilon\lambda\lambda', n_i \Lambda_i \lambda}^{KM}(R) = \sum_{I=1}^{\infty} a_I(\epsilon) \psi_{I\lambda\lambda', n_i \Lambda_i \lambda}^{KM}(R) \quad . \quad (74)$$

The set of functions, $\{a_I\}$, is characterized by

$$\sum_{I=1}^{\infty} a_I^*(\epsilon) a_I(\epsilon') = \delta(\epsilon - \epsilon')$$

$$\int_0^{\infty} d\epsilon a_I^*(\epsilon) a_J(\epsilon) = \delta_{I,J} \quad . \quad (75)$$

One can see from Equation (75) that the functions, a_I , have dimensions of $(\text{energy})^{-1/2}$. Therefore, the effective heavy particle wave functions, $\psi_{I\lambda\lambda', n_i \Lambda_i \lambda}^{KM}$, introduced as

the expansion coefficients in Equation (74), have dimensions compatible with heavy particle wave functions associated with bound state-bound state transitions, $\psi_{n\Lambda\lambda', n_i \Lambda_i \lambda}^{KM}$. The advantage to the expansion of Equation (74) is that integrals over the continuum variable, ϵ , can be replaced by summations over the discrete set of functions of ϵ . Formally, these are infinite summations. However, in the same way a small number of discrete electronic states are singled out as the important ones for some collision process, Equation (74) allows more easily the possibility of selecting a limited number of terms in the expansion which may be the most significant for the dynamics of a collision process.

With the use of Equation (74) in Equations (68) and (73), and multiplying Equation (73) by $a_{\mathbf{I}}^*(\epsilon')$ and integrating over ϵ' , the following set of coupled equations results:

$$\begin{aligned} & \{ (1/2m) d^2/dR^2 - K(K+1)/2mR^2 + E \} \psi_{\mathbf{q}', q_i}^{KM}(R) \\ &= \sum_{\mathbf{q}} \{ V_{\mathbf{q}', \mathbf{q}}^{\text{Coul}}(R) + V_{\mathbf{q}', \mathbf{q}}^{\text{BO}}(R) \} \psi_{\mathbf{q}, q_i}^{KM}(R) \\ &+ \sum_Q \{ V_{\mathbf{q}', Q}^{\text{Coul}}(R) + V_{\mathbf{q}', Q}^{\text{BO}}(R) \} \psi_{Q, q_i}^{KM}(R) \quad , \end{aligned} \quad (76)$$

and

$$\begin{aligned}
 & \{ (1/2m) d^2/dR^2 - K(K+1)/2mR^2 + E \} \psi_{Q', q_i}^{KM} (R) \\
 &= \sum_q \{ v_{Q', q}^{Coul} (R) + v_{Q', q}^{BO} (R) \} \psi_{q, q_i}^{KM} (R) \\
 &+ \sum_Q \{ v_{Q', Q}^{Coul} (R) + v_{Q', Q}^{BO} (R) \} \psi_{Q, q_i}^{KM} (R) \quad . \quad (77)
 \end{aligned}$$

In these coupled equations abbreviated notation has been introduced; $q = (n\lambda\lambda)$ labels a discrete electronic state and $Q = (I\Lambda\lambda)$ labels a "discrete", effective state associated with some region of electronic configuration space in the continuum. The $q'-q$ coupling terms in Equation (76) are simply those of Equations (69)-(72). The other coupling terms are given as follows:

$$\begin{aligned}
 v_{q', Q}^{Coul, BO} (R) &= \int d\epsilon v_{n'\Lambda', \eta\Lambda}^{Coul, BO} (R) a_I (\epsilon) \\
 v_{Q', q}^{Coul, BO} (R) &= \int d\epsilon' a_{I'}^* (\epsilon') v_{\eta'\Lambda', n\Lambda}^{Coul, BO} (R) \\
 v_{Q', Q}^{Coul, BO} (R) &= \int d\epsilon' \int d\epsilon a_{I'}^* (\epsilon') v_{\eta'\Lambda', \eta\Lambda}^{Coul, BO} (R) a_I (\epsilon) \quad , \quad (78)
 \end{aligned}$$

where the coupling terms inside the integrals are determined according to Equations (69)-(72). Equations (76) and (77) constitute a modified set of coupled equations resulting from the discretization procedure of Equation (74).

3. Solution of the Modified Coupled Equations

As was pointed out in the previous section, the effective heavy particle wave functions associated with transition from a discrete electronic state to an effective continuum electronic state have dimensions compatible with those of the bound state-bound state heavy particle wave functions. Therefore, the coupled equations of Equations (76) and (77) may be combined into a single set of coupled equations corresponding to scattering in a "discrete" set of effective electronic states which span both discrete and continuum parts of electronic configuration space. One may introduce the label p which ranges over the previous labels $q_1, q_2, \dots, Q_1, Q_2, \dots$. Then Equations (76) and (77) may be written as a single matrix equation:

$$\left\{ \underline{I} \left\{ (1/2m) d^2/dR^2 - K(K+1)/2mR^2 + E \right\} - \underline{V}^{\text{Coul}}(R) - \underline{V}^{\text{BO}}(R) \right\} \underline{\psi}^{\text{KM}}(R) = \underline{0} \quad (79)$$

Here, $\underline{I}$ is the unit matrix and

$$\underline{V}^{\text{Coul}, \text{BO}}(R) = \left(V_{p, p'}^{\text{Coul}, \text{BO}}(R) \right) \quad , \quad (80)$$

where the coupling matrix elements are those of Equation (78), and

$$\underline{\psi}^{\text{KM}}(R) = \left(\psi_{p, p'}^{\text{KM}} \right) \quad . \quad (81)$$

In Equation (81), the index p' ranges only over the labels $q_1, q_2, \dots$ of the discrete electronic states, whereas p ranges over all the labels (q_i, Q_i) . This is because in ionization processes the initial channel considered is associated with a discrete electronic state from which transition to the continuum (or also to another discrete electronic state if ionization does not occur) takes place during collision. Therefore, only wave functions for heavy particle motion associated with bound-to-bound or bound-to-continuum transitions are considered.

Equation (79) is solved by integrating the coupled second-order differential equations for the solutions which fulfill scattering boundary conditions. In what follows, only so-called open channels of the heavy particle motion are considered. That is, only those discrete and effective continuum electronic states are considered for which the relative kinetic energy of the heavy particles is asymptotically greater than zero. For channel p this asymptotic relative kinetic energy is expressed in terms of κ_p , where

$$(1/2m)\kappa_p^2 = \lim_{R \rightarrow \infty} \{E - V_{pp}^{\text{Coul}}(R)\} \quad . \quad (82)$$

To treat the open channel asymptotic boundary conditions, the Ricatti Bessel functions,

$$\mu_\ell(x) = \sqrt{\pi x/2} J_{\ell+1/2}(x) \underset{x \rightarrow \infty}{\sim} \sin(x + \ell\pi/2) \quad ,$$

and Neumann functions,

$$v_{\ell}(x) = \sqrt{\pi x/2} J_{-\ell-1/2}(x) \underset{x \rightarrow \infty}{\sim} \cos(x - \ell\pi/2) \quad , \quad (83)$$

are introduced, along with the diagonal matrices $\underline{M}_{Ln}^S(R)$ and $\underline{M}_{Ln}^C(R)$ having diagonal elements $\mu_{Ln}(\kappa_p R)$ and $v_{Ln}(\kappa_p R)$, respectively.

Then, upon integrating the coupled equations of Equation (79) into the asymptotic region ($R \gg 1$), the matrices, $\underline{X}_{KM}$ and $\underline{Y}_{KM}$, are determined from the scattering boundary conditions,

$$\underline{\psi}^{KM}(R) \underset{R \rightarrow \infty}{\sim} \underline{M}_{Ln}^S(R) \underline{X}_{KM} - \underline{M}_{Ln}^C(R) \underline{Y}_{KM} \quad , \quad (84)$$

for the solution, along with the derivative of the solution asymptotically. That is,

$$\begin{aligned} \underline{X}_{KM} = & \{ -(\underline{M}_{Ln}^S)' \underline{M}_{Ln}^C + \underline{M}_{Ln}^S (\underline{M}_{Ln}^C)' \}^{-1} \\ & \times \{ (\underline{M}_{Ln}^C)' \underline{\psi}^{KM} - \underline{M}_{Ln}^C (\underline{\psi}^{KM})' \} \quad , \end{aligned} \quad (85)$$

and

$$\begin{aligned} \underline{Y}_{KM} = & \{ -(\underline{M}_{Ln}^S)' \underline{M}_{Ln}^C + \underline{M}_{Ln}^S (\underline{M}_{Ln}^C)' \}^{-1} \\ & \times \{ (\underline{M}_{Ln}^S)' \underline{\psi}^{KM} - \underline{M}_{Ln}^S (\underline{\psi}^{KM})' \} \quad , \end{aligned} \quad (86)$$

where here the prime denotes differentiation with respect

to R.

From $\underline{X}_{KM}$ and $\underline{Y}_{KM}$ the so-called R-matrix is calculated as

$$\underline{R}_{KM} = \underline{\kappa}^{-1/2} \underline{Y}_{KM} \underline{X}_{KM}^{-1} \underline{\kappa}^{-1/2}, \quad (87)$$

where $\underline{\kappa}$ is the diagonal matrix having diagonal elements, κ_p . The S-matrix can be obtained from the R-matrix as

$$\underline{S}_{KM} = (\underline{I} + i\underline{R}_{KM})(\underline{I} - i\underline{R}_{KM})^{-1}, \quad (88)$$

and the T-matrix is related to the S-matrix:

$$\underline{T}_{KM} = -(i/2)(\underline{S}_{KM} - \underline{I}). \quad (89)$$

The S-matrix elements of Equation (88), $S_{KM}^{p,p'}$, are the $p \rightarrow p'$ transition probability amplitudes as a result of collisional processes treated in terms of the "channels" of the effective coupled equations of Equation (79). For electronic bound-to-bound state transitions (i.e., when both p and p' are among the electronic bound state labels, $q_1, q_2, \dots$), the S-matrix elements of Equation (88) may be used directly for calculating partial, total, and differential cross-sections. However, in the case of electronic bound-to-continuum state transitions, the physical process corresponds to transition from one of the discrete electronic states, labeled by p' ($=q'=(n'\lambda'\lambda')$),

to an actual continuum state (corresponding to an electron emitted with energy ϵ), labeled by $(\eta\Lambda\lambda)$. The S-matrix element (transition probability amplitude) corresponding to the physical process is therefore determined as the appropriate linear combination, based on Equation (74), of S-matrix elements for transition from a bound ($q = n\Lambda\lambda$) to a discretized continuum ($Q = I\Lambda\lambda$) state. Using the full labeling notation, one therefore writes

$$S_{KM}^{\eta\Lambda\lambda, n'\Lambda'\lambda'} = \sum_I a_I(\epsilon) S_{KM}^{I\Lambda\lambda, n'\Lambda'\lambda'} \quad (90)$$

Similarly,

$$T_{KM}^{\eta\Lambda\lambda, n'\Lambda'\lambda'} = \sum_I a_I(\epsilon) T_{KM}^{I\Lambda\lambda, n'\Lambda'\lambda'} \quad (91)$$

This completes the formal development regarding collisions involving both discrete and continuum internal electronic states. For collisional transition between discrete internal electronic states, the S- and T-matrix elements of Equations (88) and (89) are the necessary quantities for calculating partial, total and differential cross-sections. In the case of collisional transition from a discrete internal electronic state into the continuum, however, the S- and T-matrix elements of Equations (90) and (91) must be used. Furthermore, although the details are not included here, the earlier remarks regarding

coupling of electronic and nuclear angular momenta indicate that cross-sections from initial states of the colliding atoms to final states of the atoms would be expressed in terms of appropriate combinations of the $S_{KM}^{n\Lambda\lambda, n'\Lambda'\lambda'}$ and $S_{KM}^{\eta\Lambda\lambda, \eta'\Lambda'\lambda'}$ matrix elements. These combinations should be determined in the process of reconstructing asymptotic atomic states from appropriate linear combinations of molecular ($KM\lambda n\Lambda$ or $KM\lambda \eta\Lambda$) states.

At this point attention will be directed to the case of PI of Argon by metastable Helium, and the formalism presented thus far will serve as a convenient starting point for specific application to a collisional ionization process.

4. Characteristics of PI and AI Processes

There are a number of important features which distinguish PI and AI, and are useful to keep in mind when considering the dynamics involved in these collisional ionization processes. Several of the features will now be discussed. Reference will be made to $\text{He}^* + \text{Ar}$ collisions to illustrate these characteristic features.

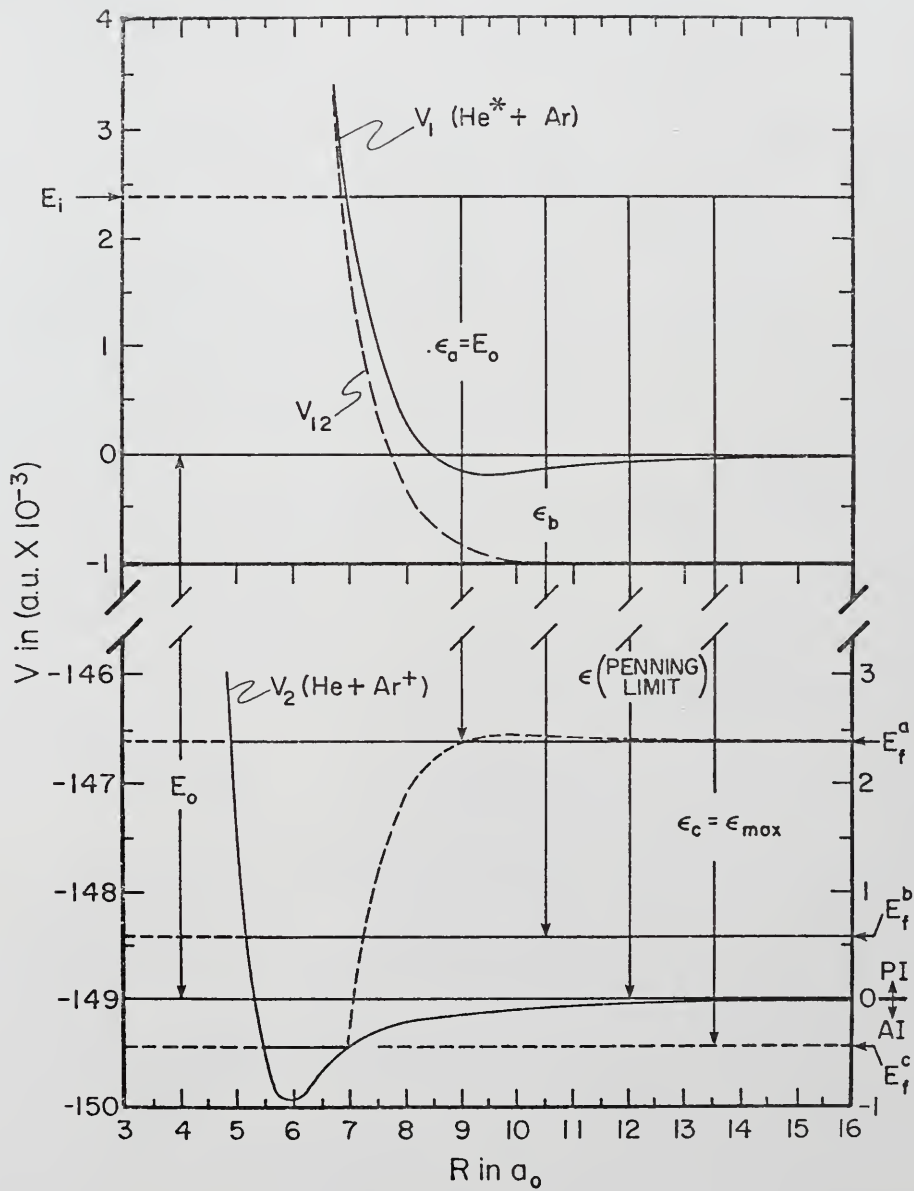
In PI and AI, the fact that the electronically excited metastable has more energy of excitation than is required to ionize its collision partner may lead to quite dramatic effects since this excess energy of electronic excitation can be as much as an order of magnitude larger than the

low (thermal) energy of relative motion of the colliding atoms. For instance, in the case of $\text{He}^*(1s2s, {}^3S) + \text{Ar}(3p^6)$, the excitation energy of He^* is 19.81 eV (see, for example, Sc73) while the ionization potential of Ar is 15.755 eV (see, for example, Mo52). Thus, in the absence of collision, the reactants ($\text{He}^* + \text{Ar}$) have 4.055 eV (≈ 0.149 a.u.) more energy than the products ($\text{He} + \text{Ar}^+$). Typical collision energies in PI and AI of Ar by He^* range, on the other hand, from 1 to 10×10^{-3} a.u., that is, around 2 orders of magnitude smaller than the asymptotic difference in channel energies. So, in PI and AI, the heavy particle motion primarily serves to bring the atoms close enough to permit the excitation energy of the excited metastable to be expended in ionizing its collision partner. In this connection, the ionization process was discussed in the previous chapter in terms of an Auger type mechanism within a molecular orbital framework. Because the relative energy of heavy particle motion is so small compared to the excess of electronic energy available for ionization, the Born-Oppenheimer coupling terms can be expected to be of negligible influence compared to the Coulomb coupling terms. In the previous chapter, it was only in the context of a united atoms analysis of molecular orbital correlation diagrams that the influence of rotational Born-Oppenheimer couplings was taken into account, because of their R^{-2} dependence.

A somewhat simplified, though very adequate, description of the dynamics of PI and AI collisions is one in which the heavy particle motion of the reactants is governed by an interaction potential of a discrete metastable molecular electronic state associated with the colliding metastable atom and its partner. In the product channel it is the interaction potential of a state of the molecular ion which governs the heavy particle motion. Most approaches to PI and AI processes have been in terms of semiempirical models relying on the width of metastable molecular states, $\Gamma(R)$, for leakage into the continuum of electronic states in which they are embedded (Na69, Mi70b, Mi71, Ol72a). In these semiempirical models, the transition into the continuum is assumed to be a Franck-Condon type process, in which the relative motion of the heavy particles is unaffected by ionization.

Much useful physical insight into PI and AI processes can be gained on the basis of these semiempirical approaches. They confirm that the emitted electrons in PI and AI are very energetic, as is known experimentally (see, for example, Ho70, Ho75, and Ce71), and as Franck-Condon type transitions would indicate. Figure 13 illustrates what basically occurs in PI and AI collisions. This figure is not just a sketch, but rather displays in quantitative detail the interaction potentials for PI and AI of Ar by $\text{He}^*(1s2s, {}^3S)$ which will be discussed and used

Figure 13. Interaction potentials and coupling for PI and AI of Ar by the $\text{He}^*(1s2s, {}^3S)$. V_1 and V_2 label, respectively, the potentials for $\text{He}^*(1s2s, {}^3S) + \text{Ar}$ and $\text{He} + \text{Ar}^+(3p^5, {}^2p)$, as described later on in the chapter, and represented by Equation (107) with the parameters of Table III. V_{12} labels a typical coupling matrix element (referred to the left scale shifted by 10^{-3} a.u.) between the discrete (metastable) state associated with V_1 and a continuum state associated with V_2 and an emitted electron of some energy ϵ , as described later on in the chapter and parameterized according to Equation (118). The energy scale on the left indicates the energy difference E_0 between the separated limits of V_1 and V_2 . E_i labels a typical thermal collision energy, and the arrows with ϵ labels are discussed in the text and illustrate a few representative energies removed by the emitted electrons, leaving the nuclei with final relative energies E_f indicated on the right and measured along a scale similar to that on the left, but referenced to the separated limit of V_2 . The lower dotted curve shows $E_f(R)$ for Franck-Condon transitions, as discussed in the text.



later on in treating the dynamics of the PI process. V_1 labels the interaction potential of the metastable molecular state, and V_2 labels the interaction potential of the molecular ion. The energy scale on the left of the figure is in accordance with the difference E_0 in energy of 0.149 a.u. between the separated reactants ($\text{He}^*(1s2s, {}^3S) + \text{Ar}(3p^6)$) and separated products ($\text{He}(1s^2) + \text{Ar}^+(3p^5, {}^2P)$). The zero of energy is arbitrary, and here assigned to the separated reactants. E_i designates a typical thermal collision energy. V_{12} labels a curve (measured against the energy scale on the left shifted by 1×10^{-3} a.u.) which reflects the expected behavior as a function of R of the Coulomb coupling between the discrete metastable state and a continuum state consisting of the state of the molecular ion plus an emitted electron which has escaped with kinetic energy, ϵ . The rate of decay into the continuum, used in semiempirical models, is proportional to $|V_{12}|^2$. These details will be taken up later in this chapter. Here, it is simply pointed out that the behavior of V_{12} in Figure 13 is in keeping with an increasing probability for transition into the continuum as the heavy particles approach their classical turning point of motion in the incident channel.

A few representative values of the amount of energy, ϵ , typically carried away by the emitted electron are indicated in Figure 13 by vertical arrows having lengths

equal to the ϵ value labeling them. The sample of ϵ values shown is merely illustrative, and there is no connection between where an arrow appears along the R axis and the probability of an electron being emitted at that R having the energy which labels the arrow. The main feature emphasized by the arrows is the range of final (asymptotic) energies of relative motion typically available to the heavy particles in the product channel. This range of energies can be measured along the energy scale at the lower right of the figure, which has the same units as the left hand scale, but references the zero of energy to the separated products, $\text{He} + \text{Ar}^+$. In the case $\epsilon_a = E_0$, the emitted electron happens to escape with exactly the energy the separated reactants have in excess of the separated products. Therefore, the final collision energy, E_f^a , in the product channel would be just the collision energy of the incident channel. That is, $E_f^a = E_i$. The ϵ_b arrow simply represents another typical value of ϵ , in a case where the final collision energy, E_f^b , is less than E_i . As will be pointed out shortly, treating the transitions as Franck-Condon in nature indicates that energies of the emitted electrons most probably have values in the neighborhood of ϵ_b , leaving the products with less energy of relative motion asymptotically than the reactants had in the incident channel. The Penning limit ϵ indicates the largest amount of energy an electron can remove for which

the heavy particles in the final channel can still (in principle) separate. The final channel is a so-called closed channel whenever an electron escapes with more energy than the Penning limit ϵ . That is, they are left with less total energy than the separated products possess. The product channel is then characterized by the heavy particles being trapped in the potential well of the electronic state of the molecular ion. The arrow labeled ϵ_c indicates such a case. It actually corresponds to the maximum amount of energy (classically) which an emitted electron could remove, and E_f^C is the final energy of relative motion of the heavy particles, which are left in some vibrational state of the product molecular ion. Indicated at the lower right of Figure 13 are the regions of PI and AI. PI, of course, occurs when emitted electrons remove energy less than the Penning limit ϵ , leaving the heavy particles with translational energy asymptotically. AI occurs when ϵ is greater than the Penning limit ϵ , leaving the heavy particles in some bound vibrational state of the molecular ion.

If the transitions were Franck-Condon in nature at each R , then the amount of final energy, E_f , left for the heavy particles upon transition occurring at each R would be as shown by the dotted curve in the bottom section of Figure 13. One can quickly arrive at an intuitive picture of the dynamics of PI and AI processes by inspecting this

"Franck-Condon" curve. It can be seen that the range of E_f is basically from E_f^C to $E_f^a = E_i$. The behavior of V_{12} indicates that the probability for transition increasingly favors transition at separations approaching the classical turning point of V_1 , i.e., R ranging from around $9a_0$ to $7a_0$. Thus one can expect the most likely final collision energies of the products to be in the neighborhood of E_f^b , as mentioned earlier.

These remarks are, of course, qualitative, but do explain trends and are confirmed by experimental measurements. They are important as guidelines for applying the formalism presented earlier in this chapter to an actual PI or AI process. One can immediately recognize that the heavy particle motion in the product channel will be associated primarily with continuum internal states confined to a narrow region of the continuum variable, ϵ . In the case of $\text{He}^*(1s2s, {}^3S) + \text{Ar}(3p^6)$, as has been seen, the range of ϵ values is of the same order as the amount of thermal collision energy of the reactants. This feature makes PI and AI well suited for discretization procedures discussed formally at the beginning of this chapter. It means that expansions, such as Equation (74), can be reliably truncated, focusing on important regions of ϵ .

One other aspect of PI and AI seen in this qualitative discussion is that the emitted electrons are very energetic. The conditions of the collisional process, in

fact, means they are more likely to escape with energy larger than the amount of excess energy available in the incident channel. As a consequence, the emitted electrons quickly escape the region of the molecular ion during collision, which means that the continuum states of the emitted electrons can well be described in terms of Coulomb waves (see Equations (62) and (63)).

5. An Application of Discretization to PI and AI

With the general background of the preceding qualitative discussion of PI and AI processes in mind, coupled equations for these processes will be derived based on the discretization formalism of the first part of this chapter. The approach here follows the basic description of PI and AI just presented, where the incident channel is represented by a single discrete (metastable) state embedded in the continuum consisting of a single final bound state of the molecular ion plus the emitted electron of energy ϵ .

Recalling the earlier remarks on nuclear and electronic angular momentum ($L_e \ll L_n$ and $\ell \ll L_n$), the electronic angular momentum is neglected as far as the coupled equations for the heavy particles are concerned. Consequently the notation of the formal development at the beginning of this chapter reduces considerably. The discretized coupled equations of Equations (76) and (77) become simply

$$\begin{aligned} \{ (1/2m) d^2/dR^2 - L(L+1)/2mR^2 \} \psi_{d,d}^L(R) + E - V_{d,d}(R) \} \psi_{d,d}^L(R) = \\ = \sum_I V_{d,I}(R) \psi_{I,d}^L(R) \end{aligned} \quad (92)$$

and

$$\begin{aligned} \{ (1/2m) d^2/dR^2 - L(L+1)/(2mR^2) + E - V_{I,I}(R) \} \psi_{I,d}^L(R) \\ = V_{I,d}(R) \psi_{d,d}^L(R) + \sum_{J \neq I} V_{I,J}(R) \psi_{J,d}^L(R) \quad . \end{aligned} \quad (93)$$

Here, d labels the discrete (metastable) state of the incident channel, and I labels discretized continuum states as before. The angular momentum of the nuclei is now denoted by L . Born-Oppenheimer couplings are neglected as previously discussed. So the $V_{I,d}$, $V_{d,I}$ and $V_{I,J}$ coupling terms are the Coulomb couplings given according to Equation (78), and $V_{d,d}$ is the Coulomb coupling given according to Equation (69). In the treatment presented here, only continuum states associated with the $\ell = 0$ partial wave of the emitted electron are considered.

At this point, a simple, but physically reasonable, set of discrete functions of the continuum variable, ϵ , is introduced. Namely, the set of functions, $\{a_I\}$, used in the expansion of Equation (74) is taken to be a set of step functions in ϵ as follows:

$$a_I(\epsilon) = \begin{cases} (\Delta\epsilon)^{-1/2} & \text{for } \epsilon_I \leq \epsilon \leq \epsilon_{I+1} \\ 0 & \text{otherwise} \end{cases} . \quad (94)$$

Here the ϵ scale has been divided into equal increments of magnitude $\Delta\epsilon$, and $\epsilon_I = I\Delta\epsilon$ locates the start of the I^{th} such increment. The basis set of step functions only partially satisfies the completeness relations of Equation (75). That is,

$$\int_0^\infty d\epsilon a_I(\epsilon) a_J(\epsilon) = \delta_{I,J} , \quad (95)$$

but

$$\sum_{I=0}^\infty a_I(\epsilon) a_I(\epsilon') = \begin{cases} 1/\Delta\epsilon & \text{for } \epsilon \text{ and } \epsilon' \text{ both in some} \\ & \text{increment, } J \\ 0 & \text{otherwise} \end{cases} . \quad (96)$$

In terms of this step-function basis set, and referring to Equation (78), the coupling terms $V_{d,I}$, $V_{I,d}$ and $V_{I,J}$ of the coupled equations of Equations (92) and (93) are expressed as follows:

$$\begin{aligned} V_{d,I}(R) &= (\Delta\epsilon)^{-1/2} \int_{\epsilon_I}^{\epsilon_{I+1}} d\epsilon \langle \Phi_d | H_{el} | \Phi_\epsilon \rangle \\ V_{I,d}(R) &= (\Delta\epsilon)^{-1/2} \int_{\epsilon_I}^{\epsilon_{I+1}} d\epsilon \langle \Phi_\epsilon | H_{el} | \Phi_d \rangle \\ V_{I,J}(R) &= (\Delta\epsilon)^{-1} \int_{\epsilon_I}^{\epsilon_{I+1}} d\epsilon' \int_{\epsilon_J}^{\epsilon_{J+1}} d\epsilon \langle \Phi_{\epsilon'} | H_{el} | \Phi_\epsilon \rangle . \end{aligned} \quad (97)$$

These coupling terms may be treated based on the following approximations. If the increment, $\Delta\epsilon$, is made small enough ($\Delta\epsilon \ll 1$), then,

$$\begin{aligned}
 & (\Delta\epsilon)^{-1/2} \int_{\epsilon_I}^{\epsilon_{I+1}} d\epsilon \langle \phi_d | H_{el} | \phi_\epsilon \rangle \\
 & \approx (\Delta\epsilon)^{-1/2} \langle \phi_d | H_{el} | \phi_{\epsilon_I} \rangle \int_{\epsilon_I}^{\epsilon_{I+1}} d\epsilon = (\Delta\epsilon)^{1/2} \langle \phi_d | H_{el} | \phi_{\epsilon_I} \rangle . \quad (98)
 \end{aligned}$$

As has been mentioned, the continuum wave functions here correspond to an emitted electron of energy ϵ in the presence of a single bound state of the molecular ion. If $\vec{r}_C$ locates the continuum electron, then, for $r_C \rightarrow \infty$ (i.e., the continuum electron far removed from the molecular ion), one may make the following approximation:

$$H_{el}(R, \vec{r}_1) \phi_\epsilon(R, \vec{r}_{N-1}, r_C \rightarrow \infty) \approx \{V^+(R) + \epsilon\} \phi_\epsilon(R) \quad , \quad (99)$$

or

$$\langle \phi_{\epsilon'} | H_{el} | \phi_\epsilon \rangle \approx \{V^+(R) + \epsilon'\} \delta(\epsilon' - \epsilon) \quad . \quad (100)$$

Here, $V^+(R)$ is the interaction potential of the molecular ion. This approximation amounts to neglecting coupling between continuum electronic states. In view of the previously mentioned fact that the continuum electronic states in PI and AI are those for which the emitted electron is very energetic, and escapes the region of the molecular

ion quickly, the approximation of Equation (100) is a reasonable one. On the basis of Equation (100), and for $\Delta\epsilon$ small, the matrix elements, $V_{I,J}$, in Equation (93) can be expressed as follows:

$$\begin{aligned}
 V_{I,J}(R) &\approx (\Delta\epsilon)^{-1} \int_{\epsilon_I}^{\epsilon_{I+1}} d\epsilon' \int_{\epsilon_J}^{\epsilon_{J+1}} d\epsilon \{V^+(R) + \epsilon'\} \delta(\epsilon' - \epsilon) \\
 &= (\Delta\epsilon)^{-1} \int_{\epsilon_I}^{\epsilon_{I+1}} d\epsilon' \{V^+(R) + \epsilon'\} \delta_{I,J} \\
 &\approx (\Delta\epsilon)^{-1} \{V^+(R) + \epsilon_I\} \int_{\epsilon_I}^{\epsilon_{I+1}} d\epsilon' \delta_{I,J} = \{V^+(R) + \epsilon_I\} \delta_{I,J} \quad (101)
 \end{aligned}$$

With these approximations, the coupled equations of Equations (92) and (93) reduce to

$$\begin{aligned}
 \{ (1/2m) d^2/dR^2 - L(L+1)/(2mR^2) + E - V_{d,d}(R) \} \psi_{d,d}^L(R) \\
 = \sum_I (\Delta\epsilon)^{1/2} \langle \phi_d | H_{el} | \phi_{\epsilon_I} \rangle \psi_{I,d}^L(R) \quad , \quad (102)
 \end{aligned}$$

and

$$\begin{aligned}
 \{ (1/2m) d^2/dR^2 - L(L+1)/(2mR^2) + E - V^+(R) - \epsilon_I \} \psi_{I,d}^L(R) \\
 = (\Delta\epsilon)^{1/2} \langle \phi_{\epsilon_I} | H_{el} | \phi_d \rangle \psi_{d,d}^L(R) \quad . \quad (103)
 \end{aligned}$$

Recalling the previous qualitative discussion of PI and AI in terms of Franck-Condon transitions, only a narrow region

of the ϵ scale will be important for the collision dynamics. Therefore, depending on the size of $\Delta\epsilon$, Equations (102) and (103) will comprise a set of N coupled equations where N is on the order of 20. Furthermore, to a good approximation, this set of N coupled equations may be replaced by N sets of two-channel coupled equations essentially by assuming that each $I \rightarrow d$ transition occurs independently of the others.

Thus, by a series of reasonable approximations in the context of a discretized set of coupled equations, it is possible to describe the collision dynamics of PI and AI in terms of several sets of two-channel coupled equations:

$$\begin{aligned} & \{ (1/2m) d^2/dR^2 - L(L+1)/2mR^2 + E - V_{d,d}(R) \} \psi_{d,d}^L(R) \\ &= (\Delta\epsilon)^{1/2} \langle \Phi_d | H_{el} | \Phi_{\epsilon_I} \rangle \psi_{I,d}^L(R) \quad , \\ & \{ (1/2m) d^2/dR^2 - L(L+1)/2mR^2 + E - V^+(R) - \epsilon_I \} \psi_{I,d}^L(R) \\ &= (\Delta\epsilon)^{1/2} \langle \Phi_{\epsilon_I} | H_{el} | \Phi_d \rangle \psi_{d,d}^L(R) \quad . \end{aligned} \quad (104)$$

Though approximate, this approach goes beyond semiempirical model approaches, which treat the heavy particle motion only in the presence of the interaction potential of the incident channel metastable state. Here, for a given transition into the continuum, the heavy particle motion is considered in both the incident and final channels, and

these are appropriately coupled by the matrix element of the electronic Hamiltonian between the discrete and discretized continuum internal states.

On the basis of the coupled equations of Equation (104), not only can total ionization cross-sections be calculated, but in the process, partial cross-sections as a function of the energy of the emitted electron are obtained. Thus one can study quantitatively the details of the energy distribution of ionized electrons in PI and AI processes. In the remainder of this chapter, an application of the coupled equations of Equation (104) to PI of Ar by $\text{He}^*(1s2s, {}^3S)$ will be presented.

6. Interaction Potentials for $\text{He}^*(1s2s, {}^3S) + \text{Ar}$ and $\text{He} + \text{Ar}^+(3p^5, {}^2P)$

Suitable interaction potentials for the reactants and products are of course required before one can proceed with solving the coupled equations of Equation (104). In this work, convenient parameterized functional forms for these potentials are introduced which describe their behavior over the whole range of internuclear separations, R .

An interaction potential is characterized by its behavior in three important regions of R ; namely, the region of short range repulsion, the region of long range van der Waals attraction, and the region of the attractive potential well. These three behaviors should be reproduced as accurately as possible in representing an interaction

potential by a parameterized functional form.

The short range repulsion typically has Born-Mayer ($Ae^{-R/b}$) behavior. This is confirmed by information on the repulsion extracted from scattering experiments as well as by electronic structure calculations, as discussed in Chapter II (see, for instance, Table I). Note that in Chapter II the form of the Born-Mayer potential, Ae^{-bR} , was used. So in this chapter, b refers to the inverse of the b of Chapter II. In Chapter II it was pointed out that the MSX α total energy for rare gas diatoms generally leads to an overestimation of the repulsion. However, the b parameters were of reasonable magnitude. Therefore, in this work, Born-Mayer b parameters for He^*+Ar and $He+Ar^+$ are determined, in the way described for the results reported in Table I of Chapter II, from the non-spin-polarized MSX α calculations on these systems reported in the previous chapter. The Born-Mayer A parameters, which are severely overestimated by the MSX α calculations on He^*+Ar and $He+Ar^+$, are determined from other considerations, which will be discussed shortly. The appropriate long range van der Waals behavior for He^*+Ar is R^{-6} , while for $He+Ar^+$, both R^{-6} and R^{-4} behavior must be included, owing to the charge-induced dipole interaction between Ar^+ and He . Values for the C_6 and C_4 coefficients reported in the literature will be used here.

A primary consideration in representing an interaction

potential is that of joining the short range repulsion to the long range van der Waals attraction in a way which adequately describes the region of the potential minimum. The important quantities with respect to the potential minimum are its depth, ϵ_m , and its position, R_m . Often the approach taken is to splice together, from one region to the next, potential functions appropriate for each region (see, for instance, Ch74 or Na75). However, a single potential function valid over the entire range of R is convenient and desirable. In this connection, Lennard-Jones (12-6) potentials have often been used for the interaction potential of the metastable state (Ro65). However, from studies of collisional ionization of Ar by Ne*, it appears that the Lennard-Jones (12-6) potential is too repulsive, which would be of steadily worsening consequences as the collision energy increases (Ol72b). There are differing points of view, however, on this matter (Ne75). On the other hand, Morse potentials which yield the proper potential well depth and position tend to produce too soft a repulsion (Ol72a).

Toennies (To73) found that reasonable potential well depths and positions could be obtained using a single potential function over the entire range of R taken simply as the sum of a Born-Mayer repulsion and the van der Waals attraction potentials. In the present work, a potential function similar to that of Toennies, yet more flexible,

is introduced. The idea behind the potential function introduced here is to modulate the long range van der Waals attractive potential (which has, for instance, R^{-4} , R^{-6} , R^{-8} , etc. behavior) by a function which preserves the van der Waals behavior at large R , while allowing in the region of the potential well an inverse R behavior stronger than that provided by the van der Waals terms. The physical grounds for this feature is to permit a more appropriate representation of the attractive forces (which typically deviate, as R decreases, from the inverse R van der Waals behavior), thereby describing the balance between attractive and repulsive forces which are responsible for the occurrence of potential energy minima. A function well suited for such a modulation is one studied by Eckart (Ec30) to simulate a potential energy barrier:

$$f_E(R; R_0, \beta, B) = (1 + e^{-(R-R_0)/B})^{-1} \times [1 + \beta(1 + e^{(R-R_0)/B})^{-1}] \quad (105)$$

As can be seen, for $R \gg R_0$, $f_E \rightarrow 1$, for $R \ll R_0$, $f_E \rightarrow 0$, exponentially, and for $\beta > 0$, f_E exhibits a local maximum at $R_{\max}$ given by

$$(R_{\max} - R_0)/B = \ln\{(\beta+1)/(\beta-1)\} \quad (106)$$

The value of f_E at $R_{\max}$ is $(\beta+1)^2/4\beta$. Denoting by $V_{1r}(R)$ the long range van der Waals attractive potential,

the following potential function is introduced:

$$V(R) = Ae^{-R/b} + V_{1r}(R)f_E(R;R_0,\beta,B) \quad . \quad (107)$$

This potential function will be applied to both the $\text{He}^*(1s2s, {}^3S) + \text{Ar}$ and $\text{He} + \text{Ar}^+(3p^5, {}^2P)$ potentials. Since the effect of the local maximum in f_E is to increase the inverse R dependence of $V_{1r}(R)$, especially in the region of the minimum, R_m , of $V(R)$, the position of the local maximum of f_E will be taken to coincide with R_m . Therefore, according to Equation (106), R_0 is determined by

$$(R_m - R_0)/B = \ln[(\beta+1)/(\beta-1)] \quad . \quad (108)$$

The b parameters in the Born-Mayer repulsion will be taken from the $\text{MSX}\alpha$ calculations reported in the previous chapter, as has just been mentioned. The exponential factor, B , in the Eckart potential will be taken equal to the Born-Mayer b parameter in each case. This is reasonable, since the Born-Mayer b parameter reflects the "softness" or "hardness" of the repulsion as described in Chapter II. The exponential behavior of the modulating Eckart function is therefore taken to be the same as that of the Born-Mayer repulsion. Finally, the Born-Mayer A parameter and the Eckart β parameter are determined by the potential well conditions,

$$\begin{aligned} V(R_m) &= -\epsilon_m \\ dV(R)/dR|_{R_m} &= 0 \quad , \end{aligned} \quad (109)$$

where, for both $\text{He}^* + \text{Ar}$ and $\text{He} + \text{Ar}^+$, ϵ_m and R_m are taken from the literature. The conditions of Equation (109) specify β and A as follows:

$$\beta = (2\epsilon_m/d) - 1 + \sqrt{(\epsilon_m/d)\{(\epsilon_m/d) - 1\}}$$

$$A = b e^{R_m/b} V'_{1r}(R_m) \epsilon_m / d \quad , \quad (110)$$

where $d = -\{V_{1r}(R_m) + bV'_{1r}(R_m)\}$ and the prime denotes differentiation with respect to R .

For $\text{He}^*(1s2s, {}^3S) + \text{Ar}$, the C_6 coefficient used here is the one reported by Bell, Dalgarno and Kingston (Be68). The values for R_m and ϵ_m used are those found by Chen, Haberland and Lee (Ch74) in an analysis of the angular distributions which they measured for $\text{He}^* + \text{Ar}$ collisions. They were able to fit parameters to a Morse-Spline-van der Waals potential. The $\text{He}^* + \text{Ar}$ potential of Chen, Haberland and Lee is the one most reliably determined, although recent work by Nakamura (Na76) indicates that the potential suggested by Olson (Ol72a) may be more appropriate for $\text{He}^*(1s2s, {}^1S) + \text{Ar}$.

Potentials for $\text{He} + \text{Ar}^+$ have been determined from data on the ratio of AI to PI cross-sections, together with considerations of energy balance based on Franck-Condon transitions (Ch74, Pe75). Recently, Nakamura (Na75) has reanalyzed these results within a semiempirical framework, and proposed a new $\text{He} + \text{Ar}^+$ potential. Here the R_m and ϵ_m

values for Nakamura's $\text{He}+\text{Ar}^+$ potential have been used, as well as his value for the C_6 coefficient based on the Slater-Kirkwood formula in terms of the polarizabilities of He and Ar^+ . The $\text{He}+\text{Ar}^+$ C_4 coefficient used is the accurate (experimental) value quoted by Dalgarno (Da62). Hartree-Fock calculations have been made on $\text{He}+\text{Ar}^+$ (Si71; see also Br75), but, as for the MSX α calculations of Chapter III, these would lend information only on the repulsive behavior of the interaction potential.

Table III lists the parameters used in the interaction potentials for $\text{He}^*(1s2s, {}^3S) + \text{Ar}$ and $\text{He} + \text{Ar}^+(3p^5, {}^2P)$. The corresponding interaction potentials are the ones shown in Figure 13, and earlier referred to in the qualitative discussion of PI and AI. Olson (Ol72a) was guided in describing the repulsive interaction of He^*+Ar by comparing it to the behavior of the repulsion determined for $\text{Li}+\text{Ar}$ using appropriate sum rules and the results for the repulsive interaction in homonuclear diatoms based on Thomas-Fermi-Dirac statistical treatment of the electronic energy (Ab69). The MSX α results for He^*+Ar are quite different, giving a value of b nearly twice that of the $\text{Li}+\text{Ar}$ value (Ab69). The MSX α value of b for $\text{He}+\text{Ar}^+$ (0.532) is quite close to that calculated for $\text{He}+\text{Ar}$ (0.5435) in Chapter II, supporting the similarity between the $\text{He}+\text{Ar}$ and $\text{He}+\text{Ar}^+$ repulsive interactions.

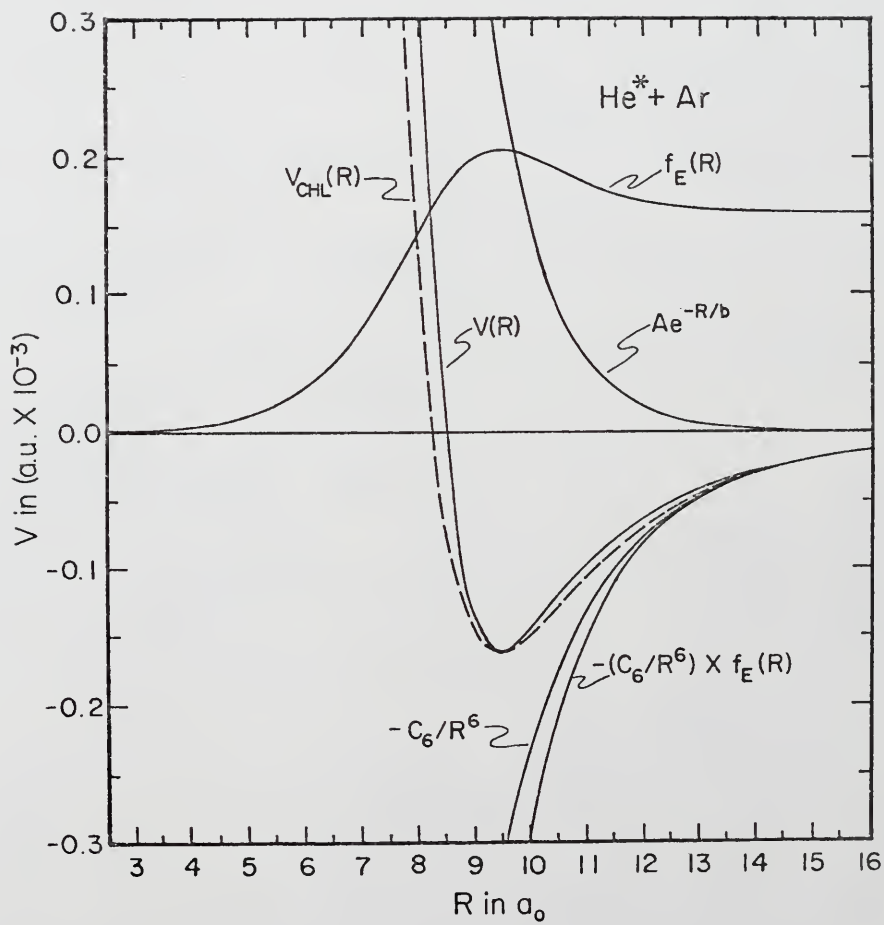
Figure 14 displays the interaction potential for

Table III. Parameters for the interaction potentials of $\text{He}^*(1s2s, {}^3S) + \text{Ar}$ and $\text{He} + \text{Ar}^+(3p^5, {}^2P)$ as given by Equation (107), where $B = b$ and R_0 is given by Equation (108). β and A are determined by Equation (110). The b parameters are from the MSX α calculations of the previous chapter.

	$\text{He}^* + \text{Ar}$	$\text{He} + \text{Ar}^+$
$A(\text{a.u.})$	4.39678	44.6527
$b(a_0)$	0.9675	0.532
$\epsilon_m(\text{a.u.})$	0.1583×10^{-3a}	0.945×10^{-3c}
$R_m(a_0)$	9.4488^a	5.936^c
$C_6(\text{a.u.})(a_0)^6$	226.0^b	7.94^c
$C_4(\text{a.u.})(a_0)^4$	—	0.6904^d
β	2.81505	6.42317

^a(Ch74); ^b(Be68); ^c(Na75); ^d(Da62)

Figure 14. $V(R)$ of Equation (107) for $\text{He}^*(1s2s, {}^3S) + \text{Ar}$ with the parameters of Table III. The various contributions to $V(R)$ as discussed in the text are indicated. $V_{\text{CHL}}(R)$ labels the corresponding potential proposed by Chen, Haberland and Lee (Ch74), shown for comparison. The Eckart potential, $f_E(R)$, is plotted against an arbitrary scale for clarity.

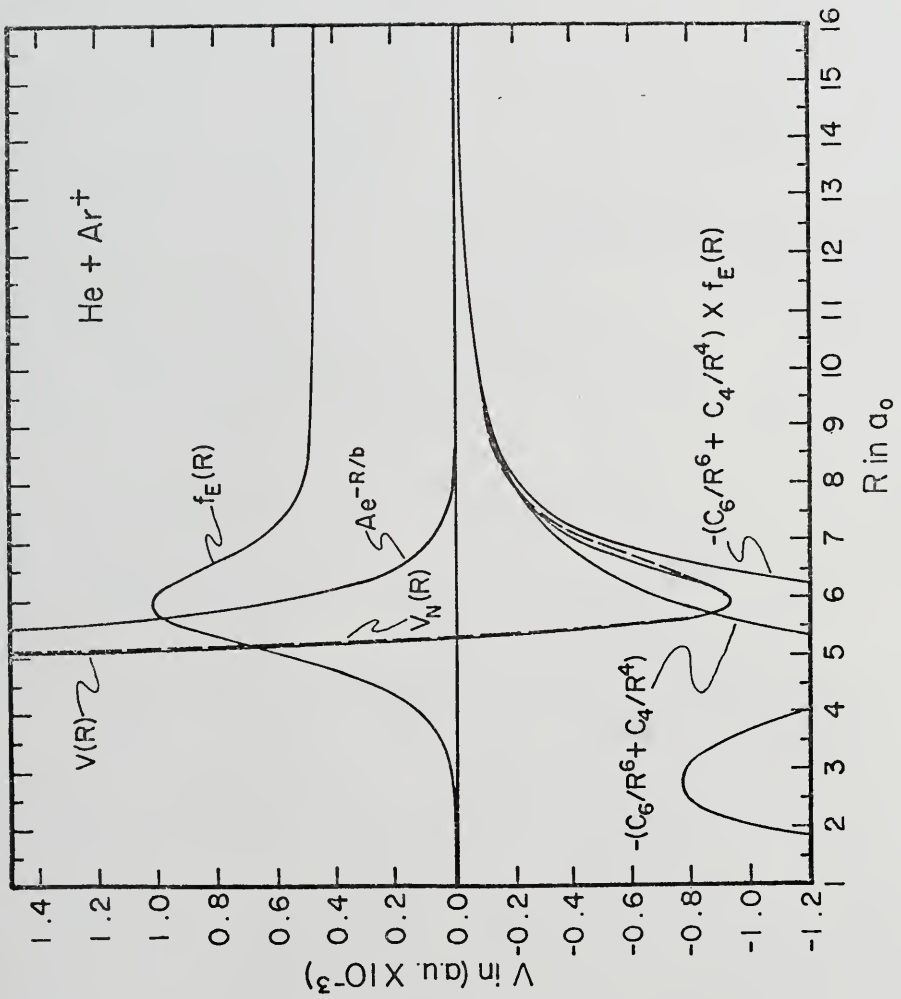


He*(1s2s,³S) + Ar represented by Equation (107) with the parameters of Table III. This is the potential labeled V_1 in Figure 13. In Figure 14, the various contributing terms of the potential of Equation (107) are shown explicitly. The deviation from R^{-6} behavior of the long range portion of the potential modulated by the Eckart potential, as well as the Eckart potential itself, are to be noted in particular. For clarity, the Eckart potential has been plotted in expanded fashion. The potential of Equation (107) shown in Figure 14 is based on well depth and position reported by Chen, Haberland and Lee (Ch74). The comparison with their Morse-Spline-van der Waals potential is quite good. The Eckart form matches their well depth conditions with a slightly stronger repulsion than provided by the Morse potential, and a slightly less attraction in the region just beyond the potential minimum.

Figure 15 is a similar plot, showing the contributions to the potential of Equation (107) for He+Ar⁺, and contrasting that potential with the one proposed by Nakamura (Na75), which joins two functional forms describing different regions of R . Again, the comparison is good, the Eckart form showing slightly weaker repulsion for the well depth and position, and first less and then more attraction for R beyond the potential minimum.

So the Eckart form of Equation (107) constitutes a very useful way to represent interaction potentials, giving

Figure 15. $V(R)$ of Equation (107) for $\text{He} + \text{Ar}^+(3p^5, 2p)$ with the parameters of Table III. The various contributions to $V(R)$ as discussed in the text are indicated. $V_N(R)$ labels the corresponding potential proposed by Nakamura (Na75), shown for comparison. The Eckart potential, $f_E(R)$ is plotted against an arbitrary scale for clarity.



a single function which can be used over the whole range of R . Of course, the Eckart form, as well as other potentials describing repulsion by a Born-Mayer function, break down as R becomes very small. This has been mentioned already in Chapter II. In addition, it will be noted that the Eckart potential tends to suppress the long range inverse R terms as $R \rightarrow 0$. However, the Eckart potential, though exponentially decreasing as $R \ll R_0$, cannot quench the inverse R dependence of the long range terms. The concave curve at the lower right of Figure 15 is part of the Eckart-modulated long range term. This behavior is not at all crucial as far as describing the interaction potential is concerned, since the exponential repulsion strongly dominates the interaction potential for R sufficiently inside of R_m to accommodate the usual range of collision energies. The important modulation effect of the Eckart potential rather is in the region around the potential minimum.

7. Parameterization of the Couplings

The interaction potentials proposed in the previous section for $\text{He}^*(1s2s, {}^3S) + \text{Ar}$ and $\text{He} + \text{Ar}^+(3p^5, {}^2P)$ provide suitably parameterized expressions for $V_{d,d}(R)$ and $V^+(R)$, respectively, appearing in Equation (104). The remaining expressions needed to solve these coupled equations are the Coulomb coupling matrix elements, $(\Delta\epsilon)^{1/2} \langle \phi_d | H_{el} | \phi_{\epsilon_I} \rangle$.

The approach here will be to rely on functional forms which have been used in semiempirical models to express the width $\Gamma(R)$ associated with the rate of decay of the discrete (metastable) state into the continuum.

The width $\Gamma(R)$ for decay of a discrete state ϕ_d into a continuum state ϕ_e degenerate with it, can be expressed as (see, for instance, Na69 or Mi70b)

$$\Gamma(R) = 2\pi |\langle \phi_d | H_{el} | \phi_e \rangle|^2, \quad (111)$$

and has units of energy in view of the fact that ϕ_e is a continuum state normalized to unity on the energy scale, as described earlier. If the transition has been of the Franck-Condon type at separation R , then in Equation (111), one must take $\epsilon = V_{d,d}(R) - V^+(R)$. In semiempirical approaches, parameterized forms for $\Gamma(R)$ have been proposed (Ho70, Ol72a, Mi71, Il75, Na75). The functional form adopted most often has been the simple exponential, namely,

$$\Gamma(R) = A_\Gamma e^{-R/a_\Gamma}. \quad (112)$$

This functional form appears to represent well the behavior of $\Gamma(R)$ as determined from both experimental and theoretical analysis (see, for instance, Ni73 or Ho70, and references therein).

In view of Equations (111) and (112), the coupling matrix element itself can be expressed in a simple exponential form, which should be a valid representation,

considering the extent to which Equation (112) has been successful in semiempirical approaches. In addition, the range of parameters, A_T and a_T , suggested in various semiempirical analyses will then give an idea of the parameters suitable for an exponential representation of the coupling matrix element itself.

When treating the matrix element, $\langle \phi_d | H_{el} | \phi_\epsilon \rangle$, of Equation (111), one must remember that it has an ϵ dependence as well as an R dependence. However, in semiempirical approaches, $\Gamma(R)$ is parameterized according to Equation (112) in order to account for transition at each R into continuum states of all possible ϵ . Thus, when A_T and a_T are adjusted to give semiempirical results in agreement with experiment, they reflect primarily the behavior of $\Gamma(R)$ of Equation (111) at an energy, ϵ_0 , near the most probable energy of the emitted electron (i.e., the peak of the electron energy distribution). Clearly, in the coupled equations of Equation (104), coupling matrix elements are required over the whole range of ϵ values, ϵ_T , which are important for PI and AI. So strictly speaking, one should first find the ϵ dependence of the discrete to continuum coupling matrix elements, and then use Equations (112) and (111) at ϵ_0 to determine the parameters of their R dependence.

An assessment of this ϵ dependence may be made in terms of the ϵ dependence of the continuum orbital describing the emitted electron. Namely, referring to Equation

(64), it is seen that the continuum orbital of energy ϵ , expressed according to Equation (62), asymptotically has its dominant ϵ dependence in the factor $\sqrt{2/\pi k} = \sqrt{2/\pi}/^4\sqrt{2\epsilon}$. Its other ϵ dependence appears in the argument of the sine function, which is not such a strong dependence since the sine function remains bound by ± 1 regardless of its argument. So, although the matrix element, $\langle \phi_d | H_{el} | \phi_\epsilon \rangle$, has its largest contribution from the region of configuration space near the molecule (where the emitted electron sees more than simply a Coulomb field), the ϵ dependence just mentioned should be appropriate. Basically, the assessment being made here is that, whereas the spatial behavior of the wave functions describing the emitted electrons near the molecule is not that of a Coulomb wave function, the emitted electrons are energetic and escape the region of the molecule rapidly, so that their ϵ dependence may be well represented on the basis of Equation (64).

Therefore, for each continuum state ϕ_ϵ , a state $\tilde{\phi}_\epsilon$ is introduced according to the relation,

$$\phi_\epsilon = (\sqrt{2/\pi}/^4\sqrt{2\epsilon}) \tilde{\phi}_\epsilon \quad . \quad (113)$$

Based on Equation (64), and recalling that ϕ_ϵ has units of $(\text{energy})^{-1/2}$ compared to bound wave functions, one sees that the factor in front of $\tilde{\phi}_\epsilon$ in Equation (113) has the units $(\text{energy})^{-1/2}$. One may further write,

$$\langle \phi_d | H_{el} | \phi_\epsilon \rangle = (\sqrt{2/\pi} / \sqrt[4]{2\epsilon}) \langle \phi_d | H_{el} | \tilde{\phi}_\epsilon \rangle, \quad (114)$$

where the matrix element on the right side of the equation is expected to have only weak ϵ dependence. It is this matrix element of weak ϵ dependence whose R dependence will be here expressed in exponential form:

$$\langle \phi_d | H_{el} | \tilde{\phi}_\epsilon \rangle = A_m e^{-R/a_m}. \quad (115)$$

Thus, using equations (111), (112), (114) and (115) based on a value, ϵ_0 , near the peak of the emitted electron energy distribution, one finds the appropriate expression by which A_m and a_m can be related to A_Γ and a_Γ :

$$A_\Gamma e^{-R/a_\Gamma} = (4/\sqrt{2\epsilon_0}) A_m^2 e^{-2R/a_m}. \quad (116)$$

On the basis of Equation (116), one sees that

$$a_m = 2a_\Gamma, \quad A_m = (\sqrt[4]{2\epsilon_0}/2) \sqrt{A_\Gamma}. \quad (117)$$

Recalling that $A_m e^{-R/a_m}$ expresses the weak ϵ dependent part of a coupling matrix element, the coupling matrix elements of the coupled equations of Equation (104) are, therefore, written,

$$\begin{aligned} & (\Delta\epsilon)^{1/2} \langle \phi_d | H_{el} | \phi_{\epsilon_I} \rangle \\ & \approx (\Delta\epsilon)^{1/2} (\sqrt{2/\pi} / \sqrt[4]{2\epsilon_I}) A_m e^{-R/a_m}. \end{aligned} \quad (118)$$

Values for A_m and a_m based on A_Γ and a_Γ parameters from semiempirical analyses can be found according to Equation (117).

For $\text{He}^*(1s2s, {}^3S) + \text{Ar}$ PI and AI, typical values of the emitted electron energy are around 0.1505 a.u. (Ho69, Ho74, Ch74). This is the value used in Equation (117) to compute values for A_m and a_m based on A_Γ and a_Γ as determined in several semiempirical analyses. The results are shown in Table IV. As can be seen, there is a wide range of A_m and a_m values indicated by semiempirical calculations. The results based on Olson's work (Ol72a) deviate markedly from the others. However, Olson chose to vary only the exponential factor, a_Γ , in his work, leaving $A_\Gamma = 1.0$ a.u. Basically the trends set by semiempirical work indicate an a_m value of about $0.7 a_o$ and A_m values in the range 20-100 a.u.

8. Results from Coupled Channels Calculations of $\text{He}^*(1s2s, {}^3S) + \text{Ar}$ PI Collisions

The heavy particle dynamics involved in PI of Ar by $\text{He}^*(1s2s, {}^3S)$ can now be treated in terms of the coupled equations of Equation (104) by implementing the interaction potentials and couplings just presented. These interaction potentials and a typical coupling term are shown in Figure 13, and from now on the $\text{He}^*(1s2s, {}^3S) + \text{Ar}$ interaction potential will be referred to as V_1 , or the upper potential, the $\text{He} + \text{Ar}^+(3p^5, {}^2P)$ interaction potential as V_2 , or the

Table IV. A_Γ and a_Γ values of Equation (112) reported in several semiempirical analyses as indicated, and the A_m and a_m values of Equation (115) calculated by Equation (117) with $\epsilon_0 = 0.1505$ a.u.

Semiempirical Analysis	A_Γ (a.u.)	a_Γ (a_0)	A_m (a.u.)	a_m (a_0)
(Pe75)	4000.0	0.36	23.41	0.72
(I175)	7400.0	0.357	31.85	0.714
(Na75)	73000.0	0.34	100.00	0.68
(O172a)	1.0	0.667	1.0	1.334

lower potential, and the coupling term as V_{12} .

The DeVogelaere numerical integration scheme, adapted from a version used previously in connection with other work (Mc71, Mc72), was employed to integrate two linearly independent solutions from deep within the non-classical regions inside the repulsive walls of both potentials out to the asymptotic region. There the boundary conditions for scattering are imposed and the R-matrix is calculated according to Equations (84) to (87).

One important characteristic feature of PI and AI is that the upper and lower potentials have repulsive walls which are quite far apart. As can be seen from Figure 13, the repulsive wall of V_1 falls in the range $6.5 a_0$ to $8 a_0$, whereas that of V_2 falls in the range $4.5 a_0$ to $5.5 a_0$, for typical incident and final collision energies, respectively. This can lead to difficulties of a numerical nature which arise in the following way.

The two linearly independent solutions which are integrated are both regular at the origin. That is, in the classically forbidden region, as R decreases sufficiently from the classical turning point of a given potential, the solution appropriate to that potential will decrease exponentially. As is normally the case, where the repulsive walls of the potentials for the various channels are in the same small range of R , all the linearly independent solutions, each appropriate for a given channel, can be specified

at a single point inside the repulsive barriers by giving them a small value (for numerical purposes, zero) and differing values for their first derivatives. As the solutions are integrated from this starting point to larger R , they increase roughly exponentially (as they should) until the classical turning point is passed (which occurs nearly simultaneously for all solutions), whereupon they exhibit typical oscillatory behavior for the classical region. For numerical reasons, even in such normal cases, the starting point cannot be chosen too deep into the non-classical region, since, even if small derivative values are assigned, the exponential increase of the solutions sustained over too many integration steps numerically becomes unstable. Neither can the integration starting point be chosen too close to the classical turning point, for then a solution may be generated which is not regular in behavior at the origin.

Numerical instability is nearly unavoidable, then, for cases such as shown in Figure 13, if a single starting point is chosen inside V_2 . The linearly independent solution appropriate to V_2 would behave properly at first, but the one appropriate to V_1 would be increasing over an unnecessarily large part of its non-classical region, becoming numerically unstable. In addition, since the two solutions are coupled, the numerical instability of one would affect the other. To avoid such numerical problems, a procedure

was introduced for suppressing the solution appropriate to the potential having the outermost repulsive wall (V_1 in Figure 13) deep inside its non-classical region where the integration for the solution appropriate to the potential having the innermost potential wall (V_2 in Figure 13) begins. As the outward integration proceeds, suppression of the one solution continues until the point inside its potential wall is reached where it satisfies the same type of starting conditions as did the solution appropriate to the inner potential wall. At that point, the suppressed solution becomes included in the numerical integration of the coupled equations with a suitable (non-classical region) starting value and derivative. Such a procedure conforms to the condition that, for R deep inside the classical turning point of a given potential, the wave function for the heavy particle motion in that potential can physically be neglected, and has led to numerically stable integration of the coupled equations.

A convenient way for simultaneously determining both suitable integration starting points and initial derivatives for a solution appropriate to a given potential was also incorporated into the calculation. The approach relies on making an estimate of the exponentially decreasing behavior of the solution, as R decreases beyond the classical turning point, in terms of a JWKB wave function in the non-classical region of the potential barrier as approximated by a linear

functional form. Such JWKB wave functions can be expressed in terms of Airy functions in the limit of large argument in the classically forbidden region. An integration step size of $1/24$ the smaller of the two channel wave lengths was found to give reliable numerical accuracy, yielding R-matrix elements differing between integration steps by only a few parts in 10^5 once the integration had proceeded into the asymptotic region to R values between two and three times the potential well position of V_1 .

Each set of coupled equations of the type in Equation (104) corresponds to transition into the I^{th} discretized continuum state. That is, referring to Equation (94), each set of coupled equations is characterized by electrons emitted with ϵ in the I^{th} interval of the partitioned energy scale. According to the earlier qualitative discussion of PI and AI, one knows which range of the ϵ scale should be important to the extent that Franck-Condon transitions occur. However, this information is not "built" into the present coupled channels approach. Rather, for given interaction potentials and coupling, the dynamics associated with electrons emitted with energy in the various ranges of ϵ can be investigated, to see what range of ϵ is indeed significant.

For the two-state problems at hand, and referring to Equation (94), the S- and T-matrix elements of Equations (90) and (91) can be simply written

$$S_{\epsilon, d}^{(L)} = \sum_I a_I(\epsilon) S_{I, d}^{(L)} \approx (\Delta\epsilon)^{-1/2} S_{J, d}^{(L)},$$

$$T_{\epsilon, d}^{(L)} = \sum_I a_I(\epsilon) T_{I, d}^{(L)} \approx (\Delta\epsilon)^{-1/2} T_{J, d}^{(L)}, \quad (119)$$

where $S_{I, d}^{(L)}$ and $T_{I, d}^{(L)}$ are the S- and T-matrix elements of Equations (88) and (89), which are found by satisfying scattering boundary conditions for the discretized set of (two state) coupled equations. In Equation (119), it is assumed that ϵ happens to be in the J^{th} interval of the ϵ scale. The partial ionization cross-section per unit energy of the emitted electron for $\epsilon + d$ transition is expressed, then, as

$$d\sigma_{\epsilon+d}(E, \epsilon)/d\epsilon = (4\pi/\kappa_d^2) \sum_L (2L+1) |T_{\epsilon, d}^{(L)}|^2. \quad (120)$$

Here, E is the incident collision energy, κ_d is given according to Equation (82), and L is the angular momentum partial wave of the heavy particles. Referring to Equation (119),

$$d\sigma_{\epsilon+d}(E, \epsilon)/d\epsilon \approx (\Delta\epsilon)^{-1} (4\pi/\kappa_d^2) \sum_L (2L+1) |T_{J, d}^{(L)}|^2, \quad (121)$$

where ϵ happens to be in the J^{th} interval as before.

The total PI cross-section is determined as follows:

$$\sigma_{PI}(E) = \int_0^{\epsilon_{PL}} d\epsilon \{d\sigma_{\epsilon+d}(E, \epsilon)/d\epsilon\} \quad (122)$$

where ϵ_{PL} is the Penning limit ϵ indicated in Figure 13.

In the present approach one may treat the integration in Equation (122) approximately as a sum, and write

$$\begin{aligned}\sigma_{PI}(E) &\approx \sum_I^{I_{PL}} \Delta\epsilon \{d\sigma_{\epsilon_I+d}(E, \epsilon_I)/d\epsilon\} \\ &\approx (4\pi/\kappa_d^2) \sum_I^{I_{PL}} \sum_L (2L+1) |T_{I,d}^{(L)}|^2, \quad (123)\end{aligned}$$

where I_{PL} refers to the last interval of the ϵ scale within the Penning limit.

The total PI cross-section of Equations (122) and (123) does not represent the entire cross-section contribution. Rather, it is the contribution from only one of the possible molecular states of the incident channel, arising from $\text{He}^*(1s2s, {}^3S) + \text{Ar}$, undergoing transition into one of the possible final continuum states, where the emitted electron has energy ϵ and the state of the $(\text{He-Ar})^+$ molecular ion separates to $\text{He} + \text{Ar}^+(3p^5, {}^2P)$. So, taking into account electronic spin and orbital angular momentum of the reactant and product atoms, the process involves 3 possible states initially and 6 finally. The total cross-section is obtained by averaging over initial states and summing over final states (see, for example, Mi75). Inherent in the present approach is the assumption that V_1 and V_2 of Figure 13 suitably represent any of the possible molecular states of the reactants or products which are compatible with their separated limits. This is a good assumption as far

as spin multiplet differences are concerned, but does not properly account for the presence of the $^2\Pi$ molecular ion state, which was found to play a role in terms of the Auger type analysis of the previous chapter. More rigorously, both the $^2\Sigma$ and $^2\Pi$ states of the molecular ion should be included, which would involve at least sets of three-state coupled equations. However, in the present approach, the heavy particle dynamics are treated only in the presence of Σ states in the initial and final channels. Averaging over initial states and summing over final states introduces a factor of 6 which should multiply σ_{PI} of Equations (122) and (123) in order to correctly assess the total PI cross-section in the framework of the present calculations.

Of interest in the study of the dynamics of the heavy particle motion are the L^{th} partial cross-sections per unit energy of the emitted electron for $\epsilon+d$ transition. These can be extracted from Equations (120) and (121), and are written

$$d\sigma_{\epsilon+d}^{(L)}(E, \epsilon)/d\epsilon \approx (\Delta\epsilon)^{-1} (4\pi/\kappa_d^2) (2L+1) |T_{J,d}^{(L)}|^2, \quad (124)$$

where again ϵ is assumed to be in the J^{th} interval. The L^{th} partial cross-section represents the contribution to the partial cross-section of Equation (121) due to L^{th} angular momentum partial wave of the heavy particles. That is, it is associated with the heavy particle motion in the effective potentials comprised of the bare interaction

potentials of Figure 13 plus the $L(L+1)/2mR^2$ centripetal potential.

In the calculations which will be reported here, $\Delta\epsilon$ was chosen to be 2×10^{-4} a.u., since it provides a reasonably fine partition of the ϵ scale. Such a $\Delta\epsilon$ divides the Franck-Condon range of electron energies (see Figure 13) into about 15 increments, which should be sufficient for probing the details of this region, which is anticipated to be of most importance.

The partial cross-section per unit energy of the emitted electron (Equations (120) and (121)) is an important quantity to monitor. Its behavior as a function of ϵ can be compared with experimental measurements of the energy distribution of emitted electrons (Ho69, Ni73, Ch74, Ho74), and therefore provides a good way of demonstrating and checking the more detailed treatment of PI which is possible in the present approach. Figures 16 and 17 display the results of calculations of $d\sigma_{\epsilon+d}(E, \epsilon)/d\epsilon$ as a function of ϵ for collision energies E of 23.89×10^{-4} a.u. (≈ 65 meV) and 15.0×10^{-4} a.u. (≈ 41 meV), respectively. These calculations were performed with coupling parameters A_m and a_m in Equation (112) of 100.0 a.u. and 0.9 a_0 , respectively. As seen in Table IV, this A_m value is the one extracted from Nakamura's work, and the a_m value lies between the first three and the one derived from Olson's work. In Figures 16 and 17, the smooth curves have been drawn through the

Figure 16. Partial ionization cross-section per unit energy of the emitted electron (Equation (121)) calculated for PI of Ar by $\text{He}^*(1s2s, {}^3S)$ at an incident collision energy $E = 23.89 \times 10^{-4}$ a.u. (≈ 65 meV), and plotted against the emitted electron energy $(\epsilon - E_0)$, top scale), or, equivalently, the relative collision energy in the final channel (E_f , bottom scale). The parameters of the coupling (Equation (118)) are $A_m = 100$ a.u. and $a_m = 0.9 a_0$. The dots are positioned at the midpoints of the increments $\Delta\epsilon$ ($\approx 2 \times 10^{-4}$ a.u.) along the ϵ scale, as described in the text.

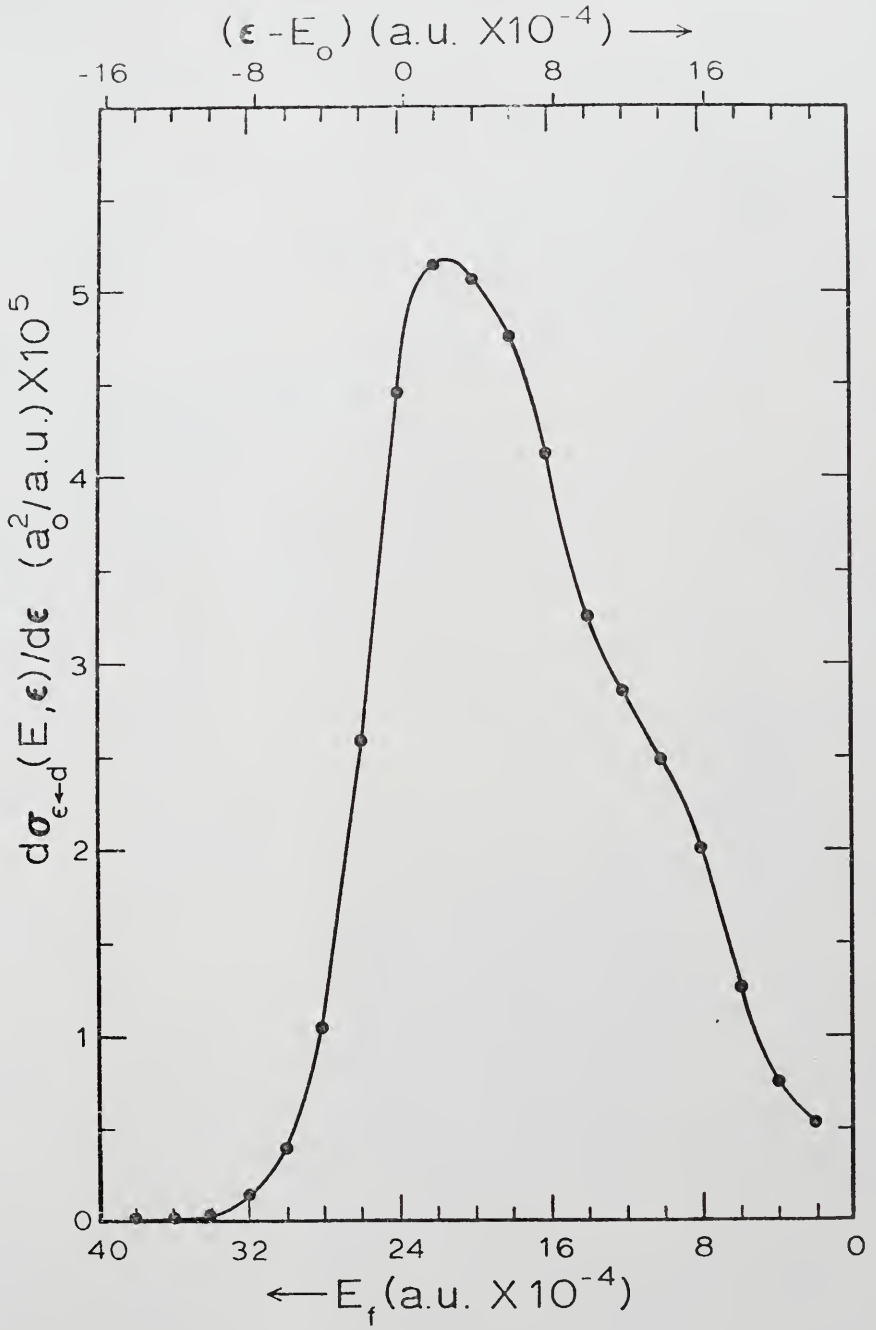
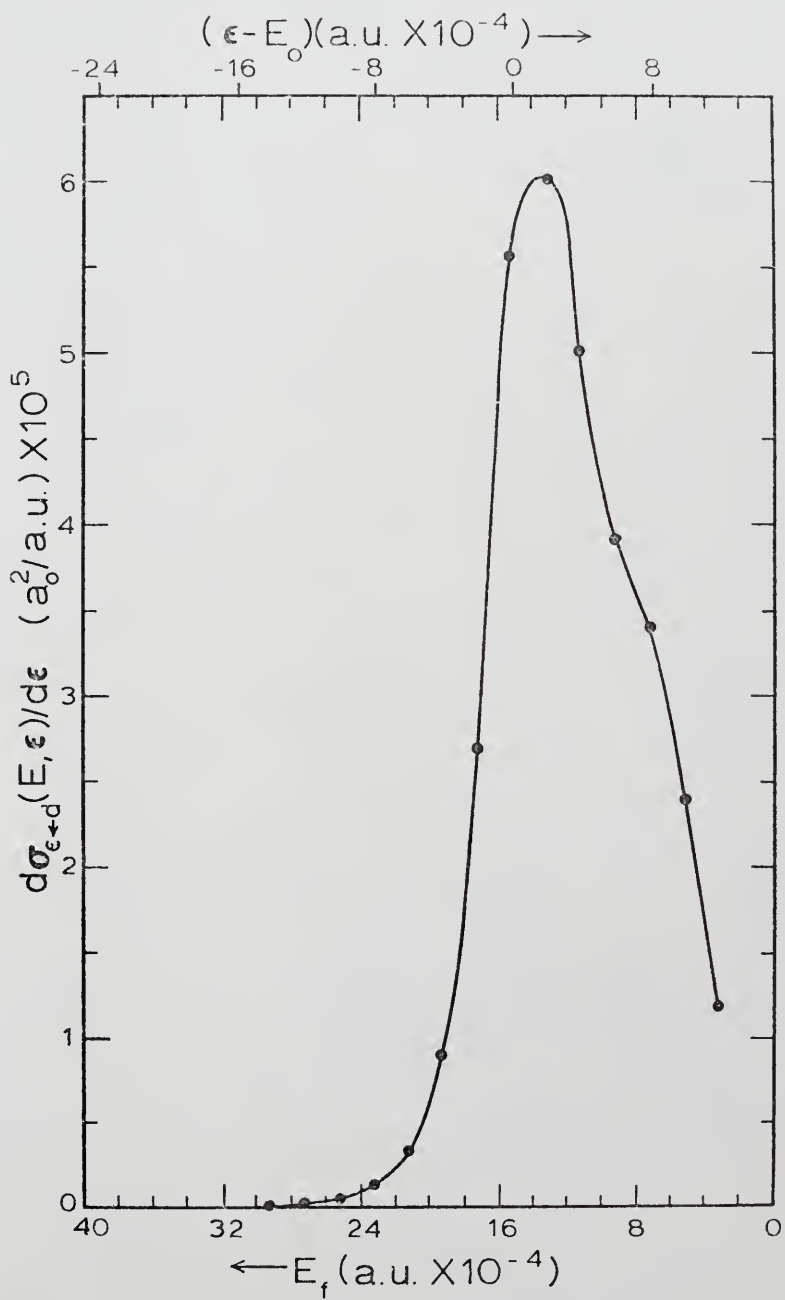


Figure 17. Partial ionization cross-section per unit energy of the emitted electron (Equation (121)) calculated for PI of Ar by $\text{He}^*(1s2s, {}^3S)$ at an incident collision energy $E = 15.0 \times 10^{-4}$ a.u. (≈ 41 meV). The details for this plot are otherwise the same as for Figure 16.



$d\sigma_{\epsilon \leftarrow d}(E, \epsilon)/d\epsilon$ values of Equation (121) at the midpoint of each increment of the ϵ scale. The ϵ dependence shown in the figures does depend on the increment size $\Delta\epsilon$, but the value 2×10^{-4} a.u. used here represents a fine enough partitioning of the ϵ scale that the ϵ dependence shown could be expected to change only slightly upon refinement of $\Delta\epsilon$.

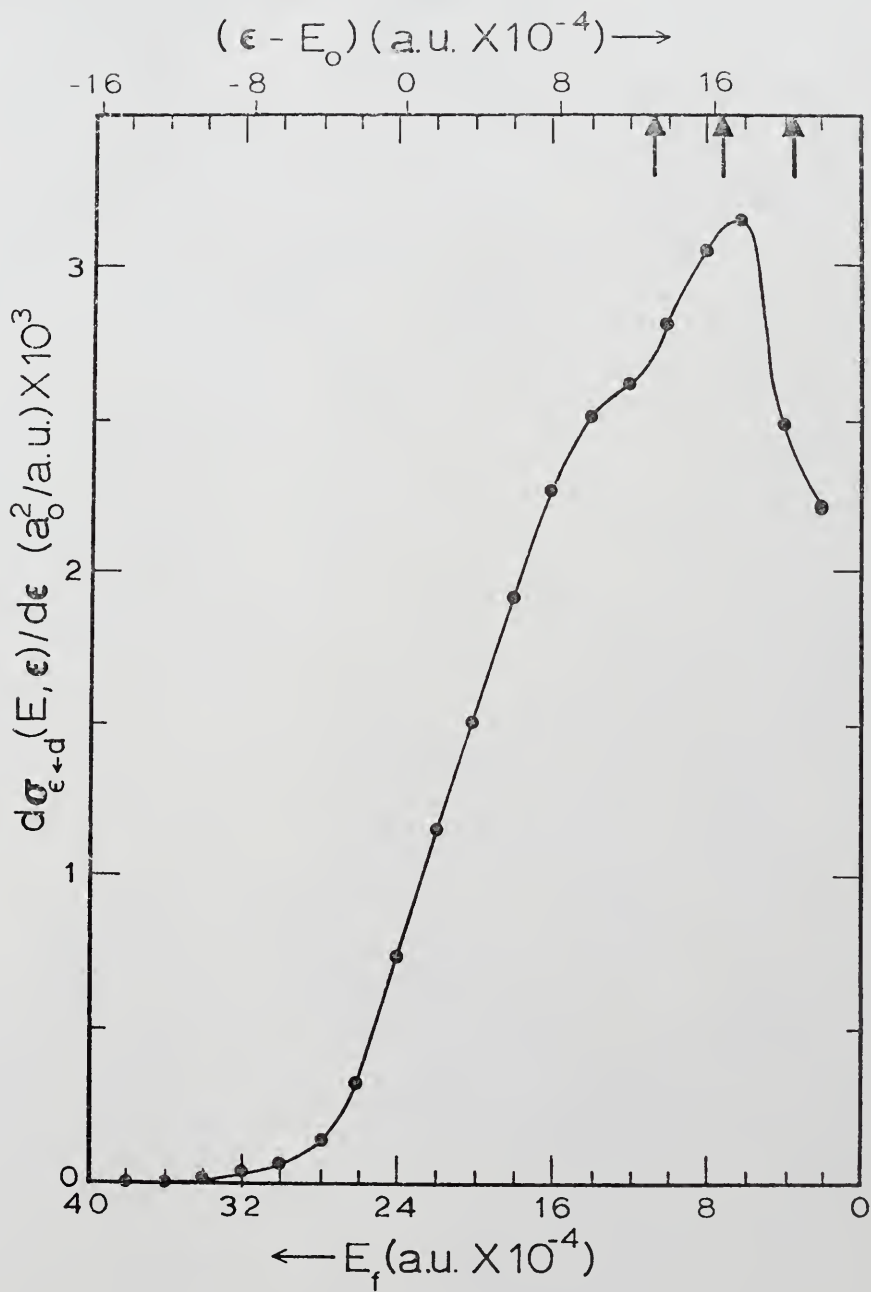
In Figures 16 and 17, the bottom scales show the collision energy of the final heavy particle motion corresponding to each ϵ of the emitted electrons, which is read along the top scales referenced to E_0 , the difference in energy between reactants and products (recall that $E_0 = 0.149$ a.u.). It is seen that the Penning limit lies at the right edge of each plot, and each curve stops just short of the Penning limit, corresponding to the last increment before entering the AI region. In order to probe the AI region, the computer program used in these calculations would have to be modified to treat both open and closed channels.

The behavior of the ϵ dependence shown in Figures 16 and 17 compares fairly well qualitatively with experimental measurements of electron energy distributions in PI and AI of Ar by $\text{He}^*(1s2s, {}^3S)$ (see, in particular, Ho69 and Ho74). The distributions in the figures peak for ϵ larger than E_0 , which is what would be expected (the reader is referred to the qualitative discussion earlier in this chapter).

However, the experimental distributions peak at values of ϵ larger still (i.e., $(\epsilon - E_0) \approx 16 \times 10^{-4}$ a.u.), favoring transitions of a Franck-Condon type much more than these calculated results. Also, not surprisingly, the experimental distributions enter the AI region having proportionately much larger contribution than those of Figures 16 and 17. Nonetheless, these calculated distributions do diminish abruptly for $\epsilon < E_0$, and the distribution at the lower collision energy shifts with respect to E_0 in the right direction (albeit very slightly), and becomes narrower, as shown by experimental results (Ho74).

The total PI cross-sections, determined according to Equation (123), for the calculations of Figures 16 and 17 are grossly overestimated, being about $4922 a_0^2$ at the higher collision energy and $3809 a_0^2$ at the lower collision energy. This certainly indicates the possibility of an inappropriate choice of the coupling parameters A_m and a_m . Figure 18 shows results for $d\sigma_{\epsilon+d}(E, \epsilon)/d\epsilon$ calculated at $E = 23.89 \times 10^{-4}$ a.u. (≈ 65 meV) with coupling parameters $A_m = 50.0$ a.u. and $a_m = 0.7 a_0$, which, referring to Table IV, are more in the range of the majority of the values extracted from semiempirical work. Figure 18 is plotted exactly as Figures 16 and 17. The ϵ dependence shown in Figure 18 constitutes a definite improvement over that of Figures 16 and 17. The peak lies nearer the experimental peaks, corresponding to a predominance of Franck-Condon type

Figure 18. Partial ionization cross-section per unit energy of the emitted electron (Equation (121)) calculated for PI of Ar by $\text{He}^*(1s2s,^3S)$ at an incident collision energy $E = 23.89 \times 10^{-4}$ a.u. (≈ 65 meV). The details for this plot are the same as for Figure 16, except here the calculations were performed with coupling parameters $A_m = 50$ a.u. and $a_m = 0.7 a_0$. The left and right arrows at the top edge of the graph locate peaks of distributions determined experimentally at $E = 36$ meV and $E = 95$ meV, respectively, and the center arrow marks the point midway between the other two, as described in the text.



transitions. Also, the distribution shows proportionately large contribution as ϵ enters the AI region. An interesting comparison can be made with experimental PI electron energy distributions reported by Hotop (Ho74). He shows distributions measured at collision energies of 36 meV, 95 meV and 125 meV. The peaks of these three distributions, in order of increasing collision energy, shift in roughly linear fashion to higher relative ϵ , being located at $(\epsilon - E_0)$ values of about 35 meV, 55 meV and 70 meV, respectively. The calculated distribution of Figure 18 is for a collision energy of 65 meV (23.89×10^{-4} a.u.), which falls nearly midway between 36 meV and 95 meV. So based on the trends shown by the experimental results of Hotop, the peak of the distribution at 65 meV should fall approximately between the peaks at 36 meV and 95 meV. Along the top right edge of Figure 18 are arrows, the left one locating the peak of the experimental distribution at 36 meV collision energy, the right one the peak of the experimental distribution at 95 meV collision energy. The calculated distribution does indeed peak nearly between the left and right arrows, indicating a good agreement with the experimental results of Hotop. The total PI cross-section for the calculations of Figure 18 is also quite reasonable, being 32.5 a_0^2 ($9.1 \text{ \AA}^2$). This value compares well with reported experimental results (see, for instance, Mu68, Ru72 or Ni73). However, little is to be gained by adjusting the

parameters A_m and a_m to reproduce certain total PI cross-section results. Rather, the calculated results of Figure 18 show that, with reasonable coupling parameters, A_m and a_m , the present coupled channels approach provides a reliable description of the PI process, reflecting well the behavior of the energy distribution of the emitted electrons, and resulting in a reasonable total PI cross-section. The A_m and a_m parameters of Figures 16 and 17 and those of Figure 18 are quite different, and yet the results of both calculations are qualitatively good, with those of Figure 18 comparing well quantitatively with experiment.

As has been mentioned, the L^{th} partial cross-section per unit energy of the emitted electron (see Equation (124)) is an interesting quantity coming out of the calculations which can give insight into some of the details of the PI process. Figure 19 shows a plot, similar in all respects to Figures 16 to 18, of the L^{th} partial cross-section per unit energy of the emitted electron for $L = 20$, where the collision energy and coupling parameters are the same as for Figure 18. The structure exhibited by $d\sigma_{\epsilon+d}^{(20)}(E, \epsilon)/d\epsilon$ as ϵ decreases from the Penning limit (i.e., as E_f increases from zero) can be understood by referring to Figure 20. In Figure 20 V_2 of Figure 13 ($\text{He}+\text{Ar}^+$ interaction potential) is plotted along with the effective potentials of the heavy particles in various angular momentum states characterized by the partial wave number, L , as indicated. Such effective

Figure 19. L^{th} partial ionization cross-section per unit energy of the emitted electron (Equation (124)) for the $L = 20$ angular momentum partial wave of the heavy particles, calculated for PI of Ar by $\text{He}^*(1s2s, {}^3S)$ at an incident collision energy $E = 23.89 \times 10^{-4}$ a.u. (≈ 65 meV). The details for the plot are otherwise the same as for Figure 18.

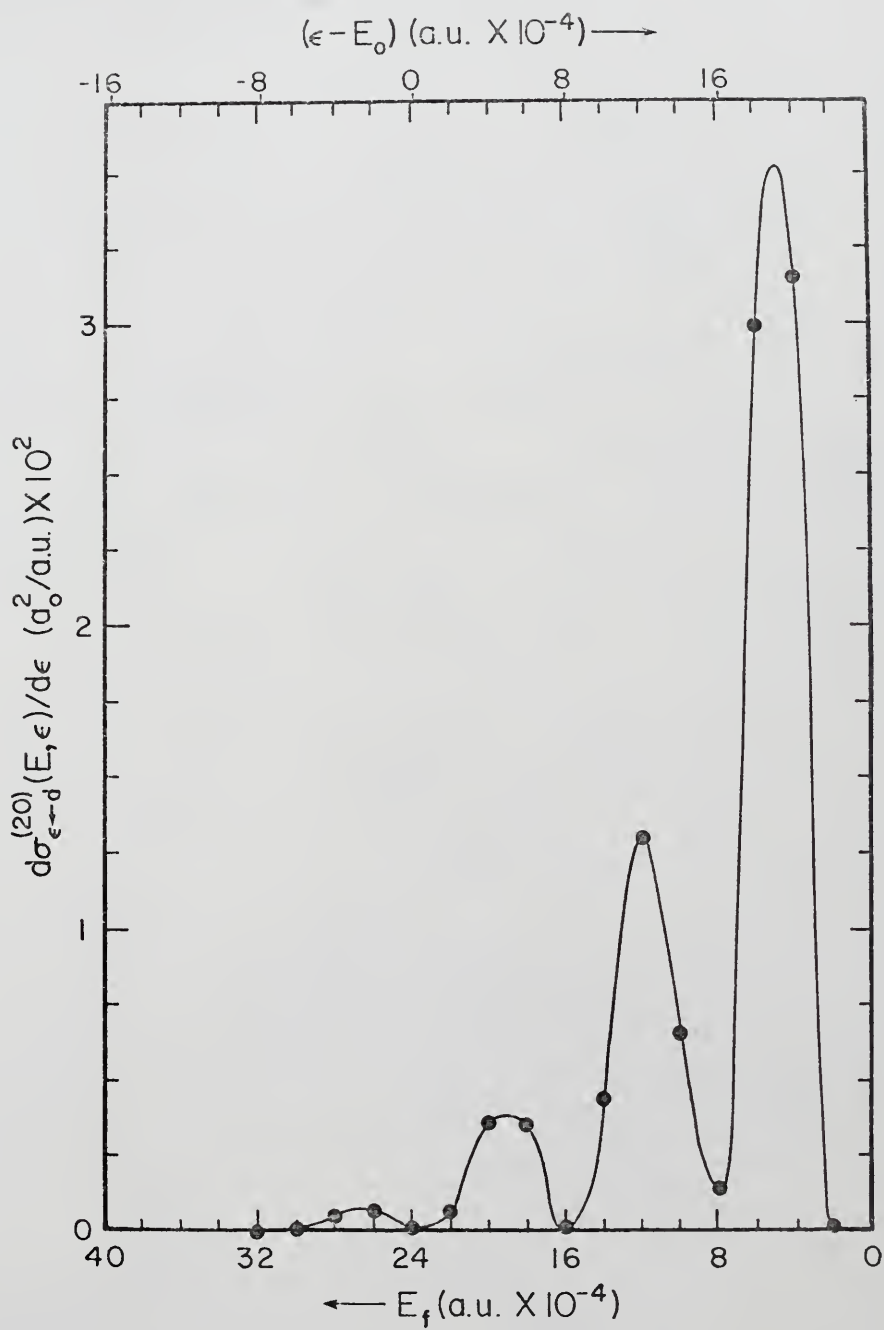
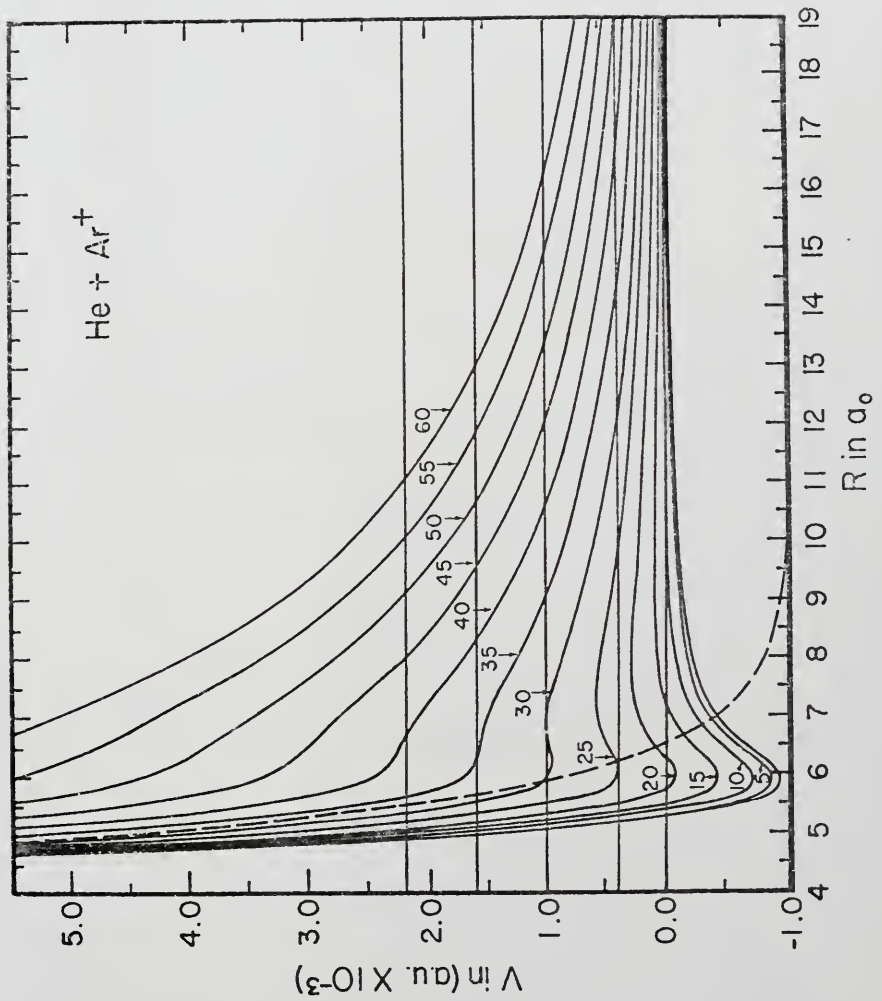


Figure 20.

Effective interaction potentials for $\text{He} + \text{Ar}^+(3p^5 2p)$. The unlabeled curve is the (bare) interaction potential previously described and shown as V_2 in Figure 13 and $V(R)$ in Figure 15. The other curves consist of the bare potential plus the centrifugal potential, $L(L+1)/2mR^2$, corresponding to the heavy particles with angular momentum partial wave number, L , for various values of L as indicated. The dotted curve is a typical coupling matrix element, shown the same way as in Figure 13.



potentials consist of the bare potential, V_2 , plus the centripetal potential, $L(L+1)/2mR^2$, and will be referred to as $V_2^{(L)}$.

The plot in Figure 19 shows, as a function of ϵ , the partial cross-section contribution for $\epsilon \leftarrow d$ transition when the heavy particles are moving in the $L = 20$ effective potentials initially and finally. Referring to Figure 20, when E_f is near zero (ϵ near the Penning limit), the heavy particles moving in $V_2^{(20)}$ see the sizable rotation barrier for $L = 20$, permitting only negligible cross-section as seen in Figure 19. But, as E_f increases (ϵ decreasing), the partial cross-section contribution exhibits a typical pattern, characterized by pronounced peaks of contribution, the first one being quite large, and each successive one increasingly smaller, until finally negligible contribution is found for E_f larger than 30×10^{-4} a.u. Looking at a particular partial cross-section as a function of E_f (i.e., of ϵ) amounts to probing the final channel continuum for a given collision energy, and detecting regions of high density of states for a given angular momentum state of the heavy particles, reflected by the resonance peaks of cross-section contribution. The large peak between 4×10^{-4} a.u. and 6×10^{-4} a.u. in Figure 19, for instance, may well be due to orbiting resonances associated with the rotational barrier of $V_2^{(20)}$, which can be seen by referring to Figure 20. Actually, in studying the detailed structure of a

partial cross-section, such as for $L = 20$ in Figure 19, it may be advisable to refine the increment size, $\Delta\epsilon$, for a more detailed look at the structure. But for studies of the over-all cross-section per unit energy, such as in Figures 16 to 18, $\Delta\epsilon = 2 \times 10^{-4}$ a.u. is sufficient for assessing the ϵ dependence.

Not only may $d\sigma_{\epsilon+d}^{(L)}(E, \epsilon)/d\epsilon$ be looked at as a function of ϵ for a given E and L , but it can be studied as a function of L for a given E and ϵ . Such results are plotted in Figures 21 to 24. All of the results in these figures are for a collision energy of 23.89×10^{-4} a.u. with $A_m = 50$ a.u. and $a_m = 0.7 a_0$. Each plot is labeled by the final collision energy E_f , prescribed by the fixed ϵ value (i.e., $E_f = E + E_0 - \epsilon$ and $E_0 = 0.149$). Pronounced resonance peaks characterize the partial cross-sections, this time as a function of L . The structure can again be understood by referring to Figure 20. The final collision energies corresponding to each plot are indicated in Figure 20 by the appropriate horizontal lines. Focusing attention on a single final collision energy, one can realize, that as L increases from 0, the specified collision energy will fall near resonance peaks, of the sort seen in Figure 19 for $L = 20$, for some of the effective potentials, $v_2^{(L)}$, and fall between such resonance peaks for other effective potentials. The largest L value for appreciable partial cross-section contribution for a given final collision energy can

Figure 21. L^{th} partial ionization cross-sections per unit energy of the emitted electron (Equation (124)) calculated for PI of Ar by $\text{He}^*(1s2s, {}^3S)$ at an incident collision energy $E = 23.89 \times 10^{-4}$ a.u. (≈ 65 meV), and plotted against the partial wave number L . The results shown are for a single energy of the emitted electron ε , with the corresponding final collision energy (given by $E_f = E + E_0 - \varepsilon$) as indicated in the figure. $E_0 = 0.149$ a.u. and the results shown are from calculations with the coupling parameters $A_m = 50$ a.u. and $a_m = 0.7 a_0$.

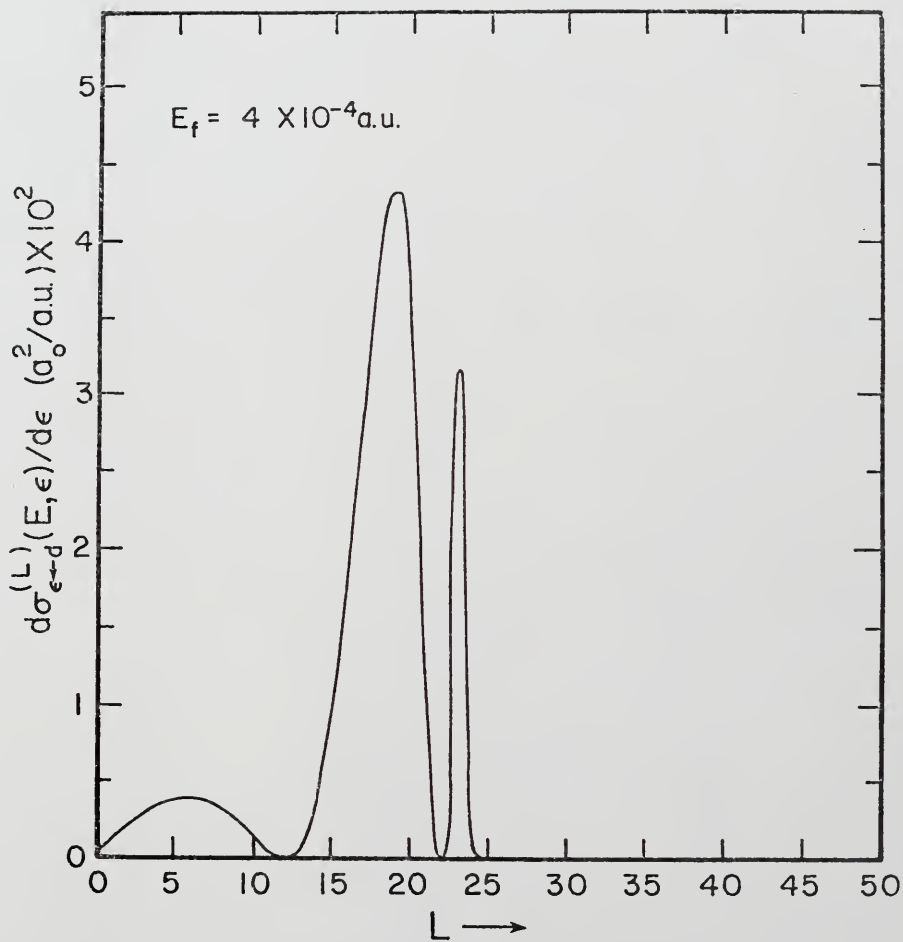


Figure 22. L^{th} partial ionization cross-sections per unit energy of the emitted electron calculated for PI of Ar by $\text{He}^*(1s2s, {}^3S)$, and plotted against L . The explanation regarding the indicated value of E_f as well as all other details for this plot is exactly as in the figure caption to Figure 21.

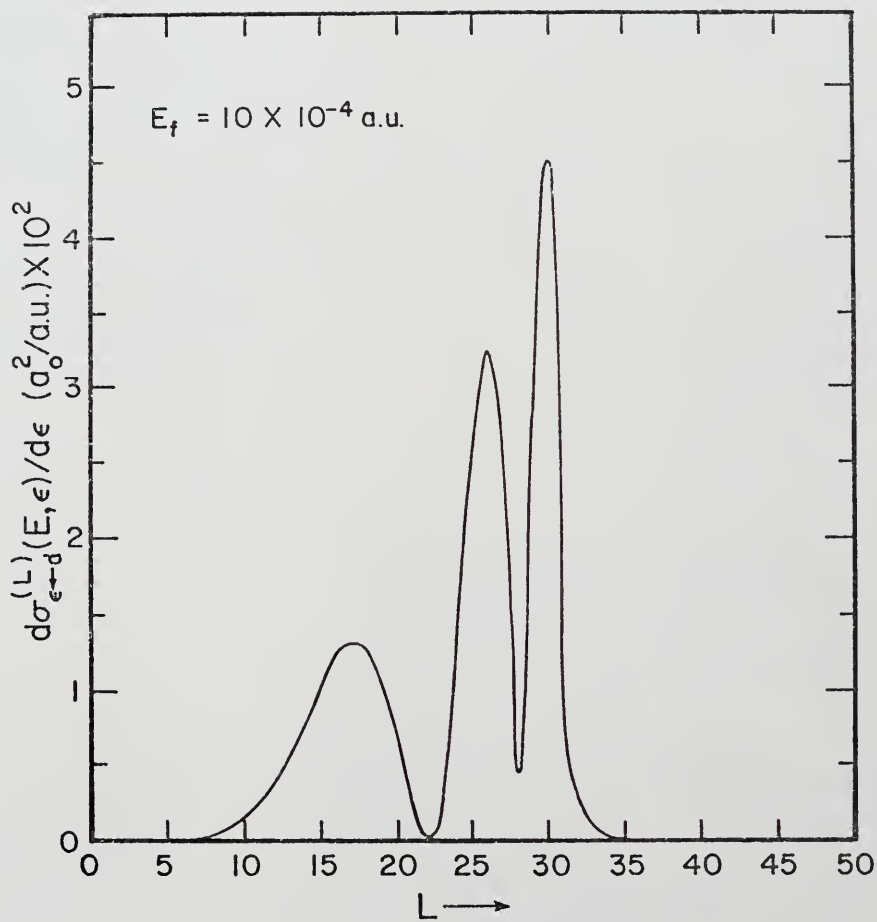


Figure 23. L^{th} partial ionization cross-sections per unit energy of the emitted electron calculated for PI of Ar by $\text{He}^*(1s2s,^3S)$, and plotted against L . The explanation regarding the indicated value of E_f as well as all other details for this plot is exactly as in the figure caption to Figure 21.

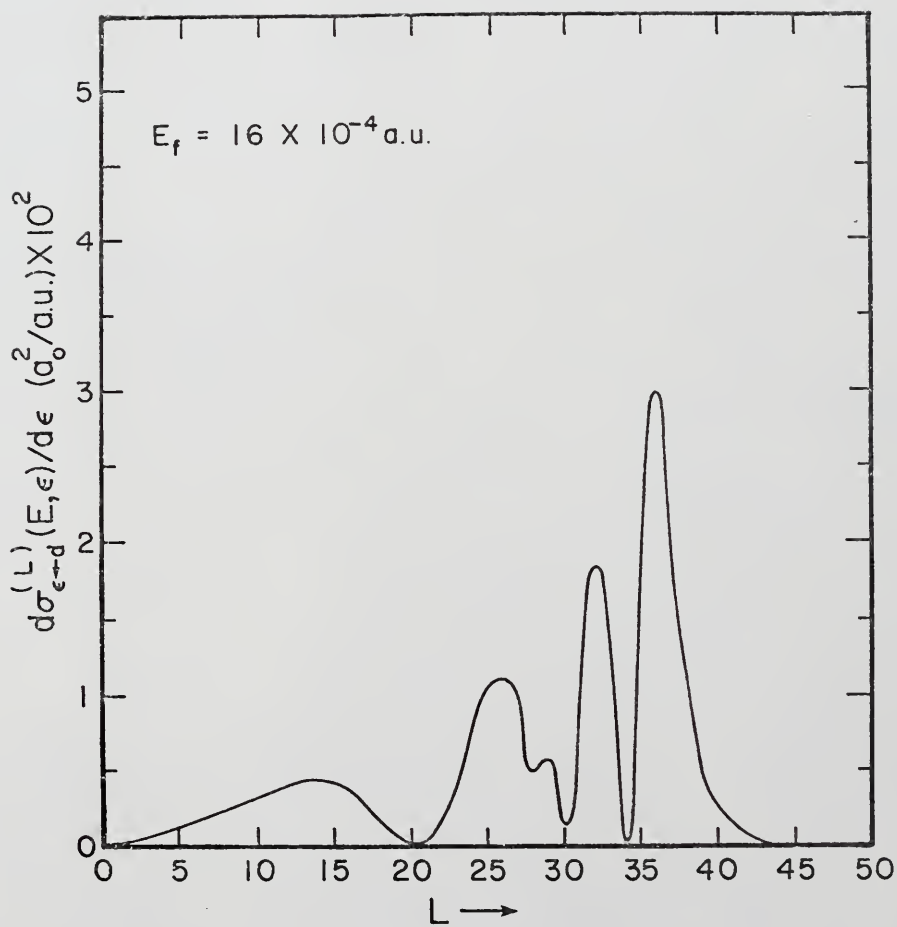
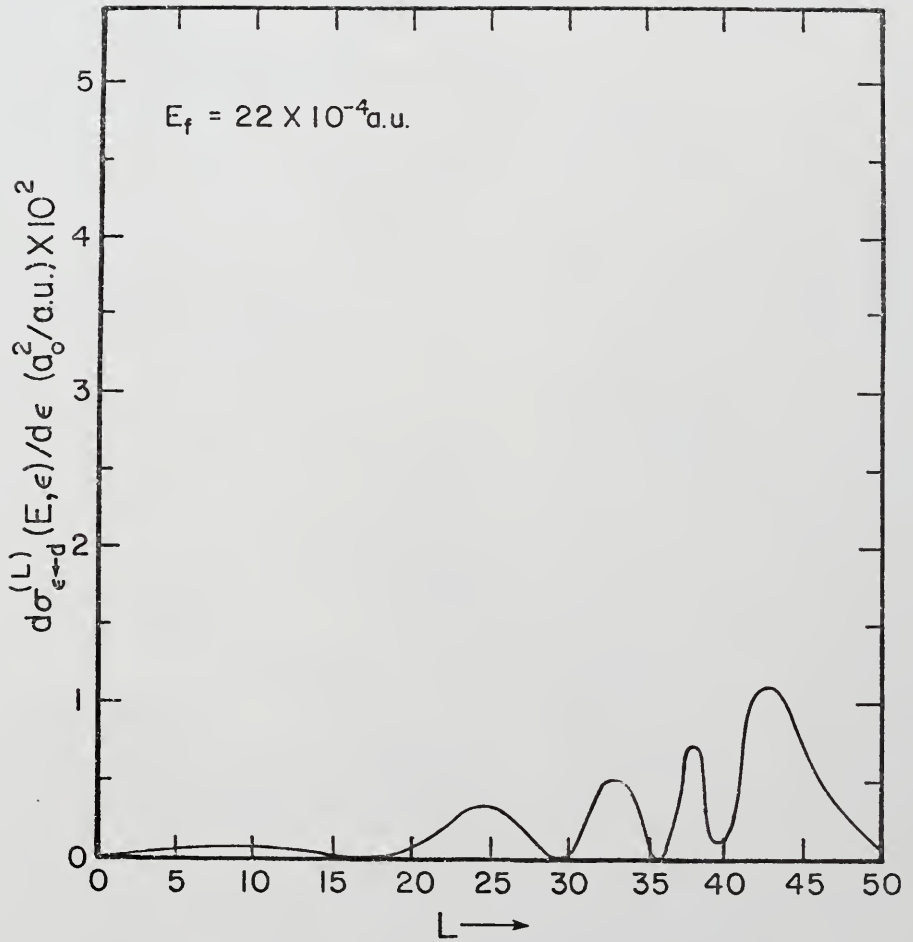


Figure 24. L^{th} partial ionization cross-sections per unit energy of the emitted electron calculated for PI of Ar by $\text{He}^*(1s2s, {}^3S)$, and plotted against L . The explanation regarding the indicated value of E_f as well as all other details for this plot is exactly as in the figure caption to Figure 21.



be readily estimated from Figure 20 by inspecting the classical turning points of the $v_2^{(L)}$ for that collision energy, and seeing for which L they begin to fall beyond the range of appreciable coupling (a typical coupling is shown by the dotted curve in Figure 20). The results shown in Figures 21 to 24 confirm such estimates, as can easily be checked. The trend as E_f increases is for the primary peaks of the structure to shift to higher L values, and in addition, for the number of peaks to increase. In Figure 21 there are two main peaks whereas in Figure 24 there are four. The results in each of the figures are characterized by a proportionately smaller and broader peak at low L values. In Figure 24, E_f is nearly as large as the initial collision energy for these calculations, and the partial cross-section contributions from all of the peaks have diminished appreciably. This, of course, would be expected from the E_f dependence of Figure 18.

9. Discussion

Formal discretization procedures, similar to those introduced in connection with continua encountered in atom + diatom collisional dissociation (Wo75) as well as in nuclear reactions (Bl66), have in this chapter been applied to the internal continuum electronic states associated with collisional ionization processes. Discretization permits one to focus more readily on the important regions

of the continuum as specified by the energy ϵ of the emitted electron, and provides a suitable framework within which to introduce and test approximate treatments of the related collision dynamics. By implementing the basis set of step functions of ϵ (Equation (94)), together with several physically reasonable approximations, it was suggested that the dynamics involved in PI and AI processes could be treated in terms of relatively few (≈ 20) two-state coupled equations, each associated with a particular small range of ϵ defined by one of the step functions.

The results of the application to PI of Ar by $\text{He}^*(1s2s, {}^3S)$ have amply demonstrated that, though approximate, this approach includes the important dynamical features of collisional ionization processes, and permits a quite adequate treatment. It goes beyond usual semiempirical models in that the heavy particle motion is governed by the interaction potential of the final state of the molecular ion as well as that of the excited (metastable) molecular state. The process of discretization allows the heavy particle motion to be calculated and distinguished according to the amount of energy ϵ removed by the emitted electron. Consequently, the partial ionization cross-section per unit energy of the emitted electron can be computed as a function of ϵ , and can be compared with experimental measurements of the energy distribution of emitted electrons (Ho69, Ni73, Ho74).

This represents an important additional level of detail in the description of collisional ionization which at the same time provides a more stringent test of the theoretical approach than is afforded by calculations of total ionization cross-sections only (see, for instance, Be74b). The results for the ϵ dependence of these distributions shown in Figures 16 to 18 show good qualitative agreement with experiment, and in the case of Figure 18, quantitative agreement is also good.

The additional feature of being able to study the L^{th} partial ionization cross-sections per unit energy of the emitted electron means that even more detail of collisional ionization processes can be monitored by looking at the cross-section contributions associated with the heavy particles moving in the various effective potentials associated with their relative rotational motion. Whether studied as a function of ϵ (Figure 19), or as a function of partial wave number L (Figures 21 to 24), their behavior reflects resonances associated with regions of high density of continuum states for the various effective potentials.

In the course of carrying out the present calculations of PI of Ar by $\text{He}^*(1s2s, {}^3S)$, a convenient functional form for atom-atom interaction potentials has been introduced (see Equation (107)). It has the nice features of representing a potential by a single function over the entire range of internuclear separations, and of having the additional flexibility provided by modulating the long range

van der Waals contribution by the Eckart function. This form for atom-atom interaction potentials is expected to be of quite general applicability.

The results reported here for PI of Ar by $\text{He}^*(1s2s, {}^3S)$ represent only a sample of what can be extracted from the calculations and analyzed as done for the results reported in Figures 19 and 21 to 24. In addition, further studies of the dependence of the results on the parameters of the interaction potentials and couplings could be made. In the present approach, reliance was placed upon the expression for the decay width $\Gamma(R)$ in terms of the coupling matrix element between the discrete and continuum electronic states (Equation (111)) in order to draw a convenient relation connecting the parameters of $\Gamma(R)$ from semiempirical work with the parameters, A_m and a_m , of the coupling matrix elements (Equation (117)). In this way, A_r and a_r values from semiempirical analyses served as useful guidelines for choosing A_m and a_m values. However, because the coupled channels calculations permit more detailed comparisons with experimental results, they would perhaps be better able to specify suitable coupling parameters, A_m and a_m , for a given set of interaction potentials, thereby providing good estimates of A_r and a_r according to Equation (118). Strictly speaking, the coupling matrix elements used for the present calculations are between the discrete (metastable) state and continuum states associated with the emitted electron in its

$\ell = 0$ angular momentum state. Couplings to components of higher ℓ should be included, but the results indicate this is not of serious consequence as far as the heavy particle dynamics are concerned.

The most interesting extension of this work would be the modification of the existing program to include the boundary conditions for closed channels. Then the coupled channels calculations for AI processes could be carried out. This would make possible a comparison with additional experimental results. For instance, the calculated distribution of partial ionization cross-section per unit energy of the emitted electron, such as shown in Figure 18, could be extended into the AI region, thereby allowing complete comparison with measured energy distributions of emitted electrons. It is anticipated that such calculated distributions in the AI region may reflect some structure associated with the vibrational states of the various effective potentials which are important.

At any rate, analyses in the AI range of ϵ could be made, similar to the one shown in Figure 19 for ϵ in the PI range. That is, by inspecting Figure 20, one could quickly determine which of the angular momentum partial waves of the heavy particles in the final channel would result in effective potentials supporting vibrational states for ϵ in the AI region. By singling out one such L^{th} partial ionization cross-section, and looking at its ϵ dependence in

the AI range, one would expect to see a structure characterized by peaks in the cross-section contribution, and reflecting the spectrum of vibrational states of the effective potential. Combining such a study in the AI range with one, such as shown in Figure 19, in the PI range, would allow one to observe, as ϵ decreased from the PI range to the AI range, first the structure associated with regions of high density of states in the continuum of the heavy particle motion, including states trapped in the rotational barrier, followed by the structure associated with the bound vibrational states of the heavy particles. Furthermore, the relative amounts of cross-section contribution among the various vibrational states in the AI region would lead to information about the distribution among final vibrational states of the $(\text{He-Ar})^+$ products in AI. This would be of interest in assessing possible mechanisms of vibrational state population inversion which may result in AI of Argon by metastable Helium.

Calculations in the AI range would also permit the comparison between the total PI cross-section σ_{PI} and the total AI cross-section σ_{AI} . Experimentally, the total ionization cross-section, $\sigma_{\text{TI}} = \sigma_{\text{PI}} + \sigma_{\text{AI}}$, and the ratio, $\sigma_{\text{AI}}/\sigma_{\text{TI}}$, have been studied as a function of the incident collision energy, E (Ch74, Ho74, Pe75, Il75). Semiempirical analyses of these quantities have also been made (Mi71, Ol72a, Ol72b, Na75, Na76). Such studies would be interesting

to carry out with the present approach, if it were extended to include ionization in the AI range.

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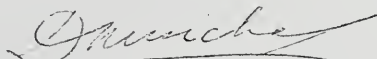
BIOGRAPHICAL SKETCH

John Curtis Bellum was born August 2nd, 1945 in Lakeland, Florida. His parents are Clifford A. and Mabel I. Bellum. He grew up in Sarasota, Florida, attending the local schools there, and graduated from Riverview High School in 1963. In the fall of the same year he entered Georgia Institute of Technology, where he received the Bachelor of Science Degree in Physics, Co-op Plan, in March of 1968.

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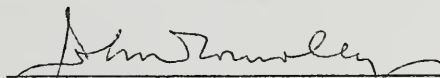
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